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Volume II. Field Validation Phase

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VALIDATION OF THE VOLATILE ORGANIC SAMPLING TRAIN (VOST) PROTOCOL
Volume II. Field Validation Phase

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16. ABSTRACT

With the development of the Volatile Organic Sampling Train (VOST) Protocol (February 1984) to measure organic emissions from hazardous waste incinerators, a wide variety of compounds have been collected and analyzed. Because its use is currently being recommended by regulatory agencies to measure emissions for compliance determinations, the VOST Protocol must be subjected to a methods validation study. The VOST validation program consists of two phases: laboratory validation studies and field test validation studies. This report documents the results of the field test validation phase.

Because of the variety of organic compounds to which this method will inevitably be applied, the almost unlimited number of permutations that could be conceived made a comprehensive validation impractical. Nevertheless, five organic compounds with boiling points in the approximate range of 30° to 100°C were chosen to be used in the validation study. They were: trichlorofluoromethane (24°C), chloroform (61°C), carbon tetrachloride (77°C), benzene (80°C) and tetrachloroethylene (121°C). This report discusses the sampling and analytical results when those five compounds were spiked into and collected from the gas stream of a hazardous waste incinerator. Precision as measured by Relative Std Deviation was less than 5%. Accuracy as measured by % recovery was about 90%.

Recommendations relative to method improvements, quality assurance measures and other aspects of VOST sampling and analysis procedures are also discussed.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Volatile Organic Sampling Train Hazardous Waste Incinerator Trace Organics		

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems for air; implementation of Agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency including the Office of Air and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

The measurement of volatile organic emissions from a hazardous waste incinerator is one of the more difficult source testing problems. Specific compounds called principal organic hazardous constituents (POHC) are to be identified and quantified at levels of 0.5 to 100 ppb in hot, wet incinerator exhaust gas, which may also contain high particulate and acid levels. The protocol, which describes the practices used by laboratories making these measurements, allows for several alternative designs and operating procedures. A methods validation program was developed to evaluate under controlled conditions in the laboratory and the field as many of the acceptable practices as possible. This report describes the laboratory phase of this methods validation program.

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Abstract

The measurement of volatile organic emissions from a hazardous waste incinerator is one of the more difficult source testing problems. Specific compounds called principal organic hazardous constituents (POHC) are to be identified and quantified at levels of 0.5 to 100 ppb in hot, wet incinerator exhaust gas, which may also contain high particulate and acid levels. The protocol, which describes the practices used by laboratories making these measurements, allows for several alternative designs and operating procedures. This paper describes an experimental program to evaluate under controlled conditions in the laboratory as many of the acceptable practices as possible. It describes the results of sampling at various concentration levels using two tube configurations, two moisture levels and other procedural variations. These results have led to conclusions about the specific VOST procedures to be followed during the field validation studies.

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SECTION 1

INTRODUCTION

A volatile organic sampling train (VOST) has been developed in recent years to measure emissions of principal organic hazardous constituents (POHC) from hazardous waste incinerators. Since its initial development, the VOST method, which includes procedures for reagent preparation, sampling, and analysis, has undergone continual revision to reach its current status as the VOST protocol.* Because of the wide variety of organic compounds involved and the relative complexity of the VOST protocol, additional methodology improvements are likely in the future. Given that a significant amount of background emission data have already been collected by use of the VOST and that its use is currently being recommended by regulatory agencies to measure emissions for compliance determinations, the VOST protocol must be validated. The Quality Assurance Division (QAD) of the U.S. Environmental Protection Agency (EPA) Environmental Monitoring Systems Laboratory (EMSL) is conducting a method validation program for this purpose. The VOST validation program consists of three phases: a laboratory validation, field testing, and interlaboratory testing.

In conjunction with the test method validation, QAD is also developing a performance audit program to enable field audits to be made of selected

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*Protocol for Collection and Analysis of Volatile POHC's Using VOST. Prepared for EPA by Envirodyne Engineers, Inc. February 1984.

POHC's during compliance trial burns. In November 1983, PEI Associates, Inc., (PEI) participated in the VOST performance audit program by conducting a laboratory audit for POHC determinations from two audit gas cylinders. PEI also conducted the VOST laboratory validation phase in the spring and summer of 1984 and is currently planning to conduct the VOST field test phase in 1985. This report documents the laboratory validation phase of this project.

The laboratory validation of the VOST procedures for sample collection and analysis was conducted in PEI's Cincinnati laboratory. A four-train (quad-train) sampling assembly was used to sample known concentrations of six volatile organic compounds (benzene, chloroform, carbon tetrachloride, tetrachloroethylene, trichlorofluoromethane, and vinyl chloride). Sample preparation, conditioning, and analyses were conducted in accordance with the February 1984 VOST protocol, with minor modifications or clarifications as described in the report.

Section 2 provides a general description of the laboratory evaluation and the project objectives. Section 3 describes the equipment used and the procedures followed and discusses how they differ from those specified in the protocol. Section 4 presents the results and data summaries. Section 5 summarizes the results and conclusions of the laboratory validation phase and presents recommendations for the field test phase. Appendix A contains calculations relevant to the statistical analysis. Appendix B contains details of sorbent trap preparation, and Appendix C contains details of the GC/MS analytical procedures. Quality assurance measures and results are presented throughout the report (where appropriate) and in Appendix D. Appendix E describes the Ruggedness Test procedures and results.

SECTION 2

PROJECT DESCRIPTION

This section describes the project objectives, the selected target compounds, the general procedures followed, and the types of experiments that were conducted.

2.1 PROJECT OBJECTIVES

The primary objectives of the validation test program were as follows:

(1) To determine the precision and accuracy of the VOST protocol for the selected compounds at two concentration levels.

(2) To use two types of sorbent trap designs (suspended tube and necked-down, described later in Figure 2-3) for sample collection and analysis to determine if the results obtained with the two configurations differ significantly.

(3) To conduct a Youden ruggedness test to determine if the variation between two levels of seven selected parameters significantly affects precision and accuracy.

(4) To determine the effect of storage time prior to analysis (holding time) on sample recovery and stability, and whether there is a significant difference between the two trap configurations in this regard.

(5) To analyze a series of sorbent traps to determine the change in blank levels with storage time and whether there is a significant difference in blank levels between the two types of trap configurations.

A secondary objective was to assess the potential for breakthrough of the target compounds, or the relative amounts of the targets collected on the first of the two sorbent traps in each sample.

The scope of this laboratory project was limited. The goal of the test program was not to make an all-encompassing evaluation of VOST sampling and analytical procedures or to develop new methods. The variety of organic compounds to which the method will inevitably be applied, the practically unlimited number of permutations that could be conceived for experimentation, and time and budget constraints made a comprehensive evaluation (or development of a new methodology) impractical, if not impossible. It was important, however, to keep an open mind and record observations during all phases of the validation program so that secondary project objectives (recommendations relative to method changes, improvements, equipment specifications, quality assurance measures, or other aspects of VOST sampling and analysis) could be accomplished.

2.2 TARGET COMPOUNDS

Six volatile organic compounds were used in the VOST laboratory validation study. The compounds listed in Table 2-1 were selected according to the boiling point range specified in the current protocol. Two of these compounds, carbon tetrachloride and chloroform, were included because of their expected frequent designation as principal organic hazardous constituents (POHC) in hazardous waste incinerator trial burns. Benzene was included because of the effect its historically high background levels has had on Tenax, which is the primary sample collection medium of the VOST. Tetrachloroethylene or perchloroethylene (commonly referred to as "perc") was included in the study to test recovery of a compound with a boiling point (121°C) near the high range of the protocol (approximately 100°C). Trichlorofluoromethane (TCFM) was selected because its boiling point (24°C) challenged the lower limit of the protocol (approximately 30°C). Except for

TABLE 2-1. LIST OF COMPOUNDS SELECTED FOR VOST PROTOCOL VALIDATION

Compound	Boiling point,[b] °C	Incinerability[a] ranking		Comments
		ΔH^c	T 99.99/2[d]	
Tetrachloroethylene	121	15	1	Group 1 compound,[e] potential recovery problem
Benzene	80	282	23	Group 1; historical Tenax blank problem
Carbon tetrachloride	77	4	2	Group 1
Chloroform	61	10	44	Group 1
Trichlorofluoromethane	24	1	NL[f]	Group 2; potential breakthrough
Vinyl chloride	-12	58	26	Group 1; potential breakthrough

[a] A ranking of 1 is the most difficult to incinerate.

[b] The general target range in the VOST Protocol is 30° to 100°C.

[c] Based on the heat of combustion table for 283 RCRA Appendix VIII constituents.

[d] Based on the temperature required to achieve 99.99 percent destruction at a residence time of two seconds (list of 55 compounds compiled by J.J. Cudahy of IT Enviroscience, September 1983).

[e] Group number refers to the QAD gas cylinder audit program.

[f] Not listed.

TCFM, mixtures of these compounds were readily available through the QAD gas cylinder audit development program. The QAD's Group 1 gases also contained vinyl chloride (VC). This compound was included in the study because of its availability as a Group 1 compound and because QAD's preliminary audit program results indicated that it could be collected and analyzed by VOST to some degree, even though its boiling point (-12°C) was well below the lower target limit of the protocol (approximately 30°C). The time frame of the project did not permit a new mixture to be made up containing all six validation compounds (i.e., adding TCFM to a Group 1 cylinder); therefore, a separate cylinder containing only TCFM and nitrogen was obtained from the same vendor that supplied the Group 1 gases.

Test gas atmospheres for the laboratory study were generated by mixing gases from a cylinder of the five Group 1 gases (approximately 75 ppb each component, balance nitrogen), a cylinder of approximately 75 ppb TCFM in nitrogen, and a cylinder of ultra-pure zero air. The cylinders containing target compounds were analyzed independently by Research Triangle Institute (RTI) to verify labeled cylinder values and the stability of the low-level gases over the duration of the project. No values differed by more than 10 percent. The dilution system used to mix the gases was checked for leaks, levels of contamination, stability of operation, and accuracy and found to be acceptable before any test samples were collected.

The dilution system and cylinder gases were used to generate nominal test gas concentrations of 15 and 0.5 ppb. These two concentrations were selected because they are believed to be within the range of normal hazardous waste incinerator concentrations, based on limited information obtained from various individuals involved in the area of VOST testing. Very little data were made available for review, however.

2.3 GENERAL APPROACH

A quad (four-train) VOST was used to collect four samples simultaneously from a manifold purged with test gas of known levels of target compounds. Figure 2-1 is a schematic of this arrangement. For tests in which moisture was added to the sample gas, only two of the four trains were operated. Changes to the equipment arrangement for moisture runs are shown in the inset in Figure 2-1. Sampling and analytical procedures for each of the four trains followed those specified in the February 1984 VOST protocol, except as documented herein. Figure 2-2 is a schematic of an individual train. Each sample represents a pair of sorbent traps: a Tenax trap connected in series with a Tenax/charcoal trap. The equipment is described in more detail in Section 3.

Both sorbent trap configurations included in the VOST protocol were evaluated to ascertain any statistically significant difference between the two. Figure 2-3 depicts PEI's version of the suspended tube (ST) type trap design [referred to as the inside/outside (I/O) configuration in the VOST protocol] and the tapered, or necked-down (ND) type of trap design [referred to in the protocol as the inside/inside (I/I) configuration]. The quad-train condensers and flasks were fabricated with joint configurations that allowed both ND and ST sorbent trap designs to be used in the sample box at the same time. Each quad-train sample run consisted of two ST type trains and two ND type trains, except for the ruggedness tests and moisture runs; for these, only two trains were operated at a given time, and both trains were of the same type, either ND or ST. The position of individual sampling train components within the quad-train system was varied between each run to eliminate any inherent bias.

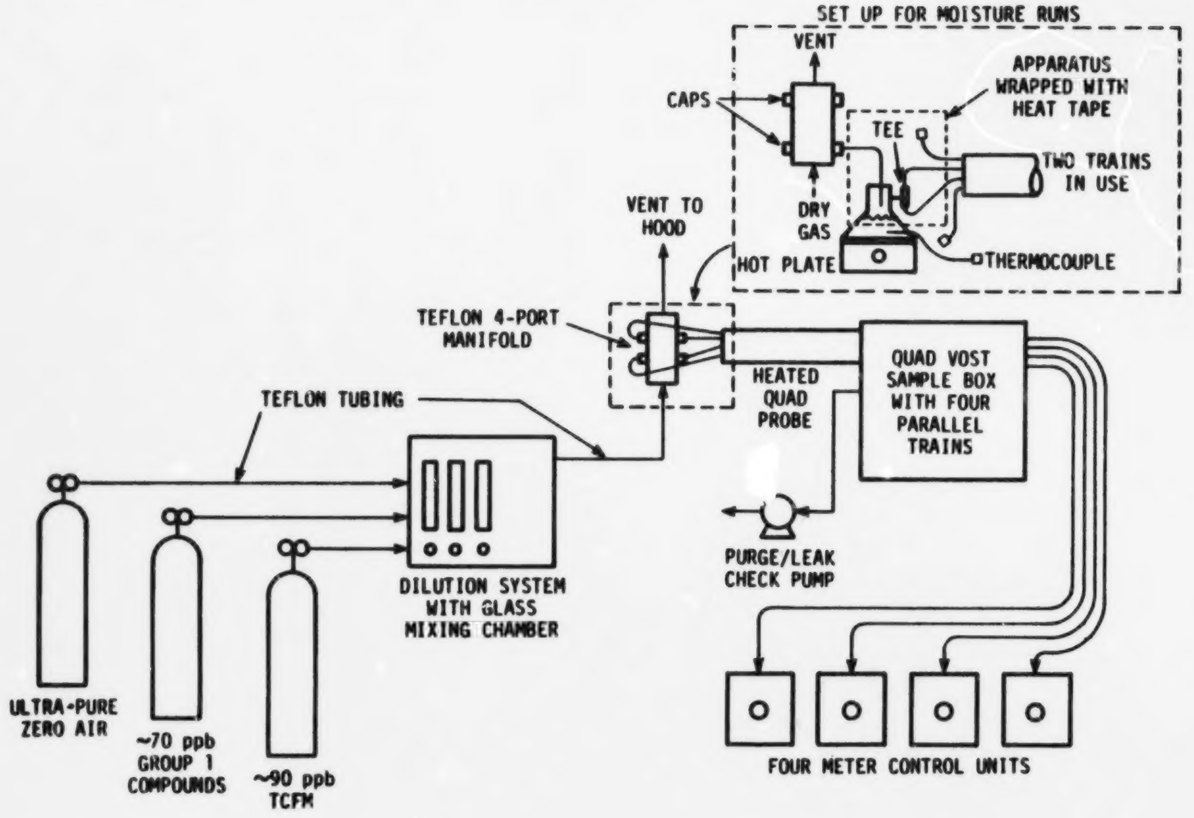
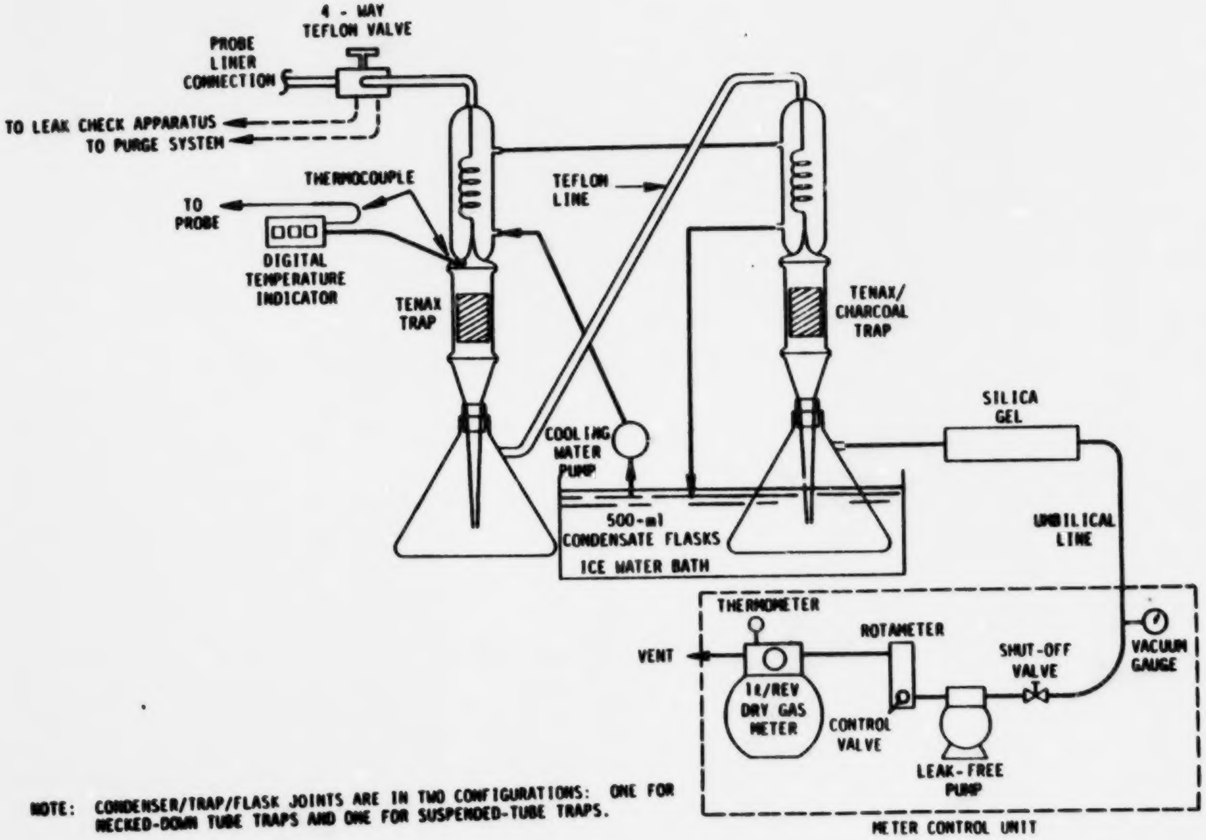
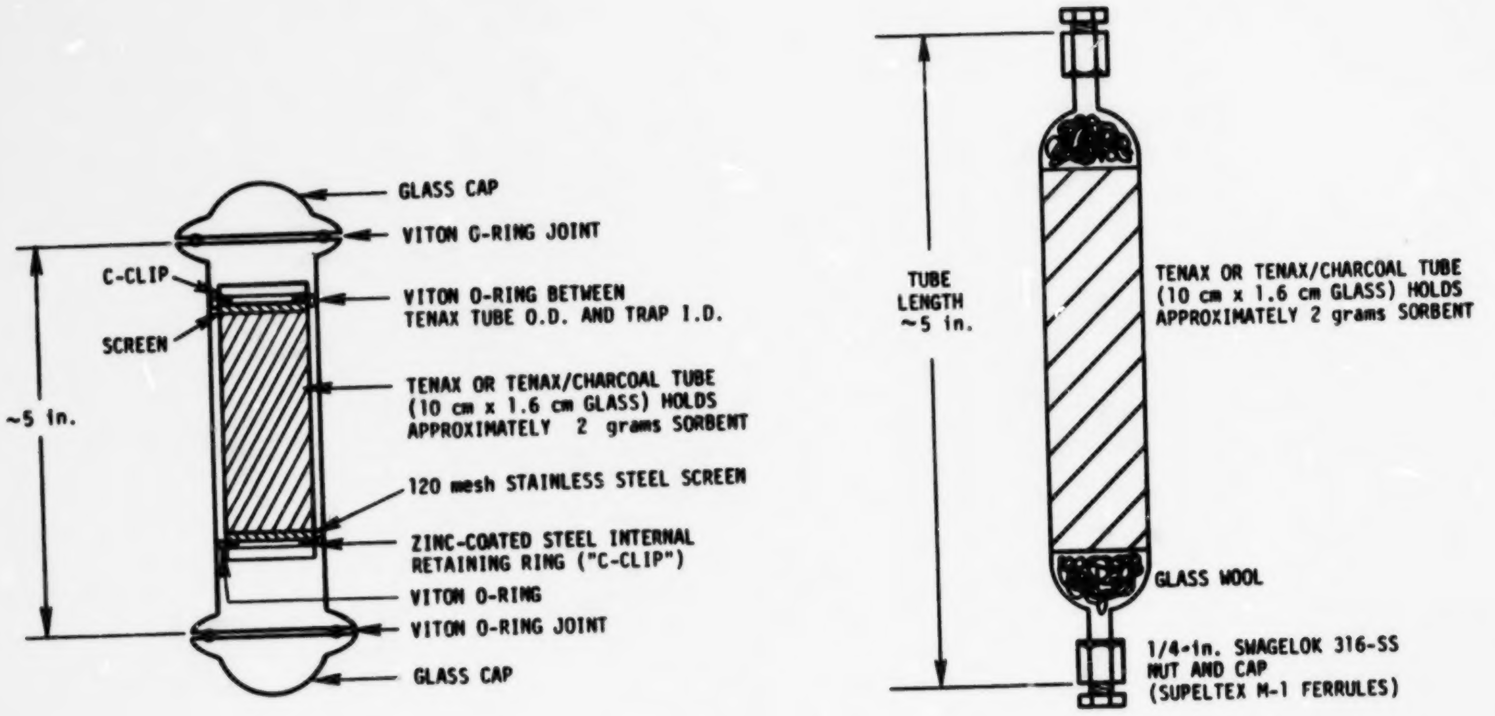

SET UP FOR MOISTURE RUNS
VENT
CAPS
APPARATUS WRAPPED WITH HEAT TAPE
TEE
TWO TRAINS IN USE
DRY GAS
VENT TO HOOD
HOT PLATE
THERMOCOUPLE
TEFLON 4-PORT MANIFOLD
QUAD VOST SAMPLE BOX WITH FOUR PARALLEL TRAINS
HEATED QUAD PROBE
TEFLON TUBING
PURGE/LEAK CHECK PUMP
DILUTION SYSTEM WITH GLASS MIXING CHAMBER
ULTRA-PURE ZERO AIR
~70 ppb GROUP 1 COMPOUNDS
~90 ppb TCFM
FOUR METER CONTROL UNITS

Figure 2-1. Schematic of sampling arrangement for laboratory evaluation.


4 - WAY
TEFLON VALVE
PROBE
LINER
CONNECTION
TO LEAK CHECK APPARATUS
TO PURGE SYSTEM
THERMOCOUPLE
TO
PROBE
DIGITAL
TEMPERATURE
INDICATOR
TENAX
TRAP
TEFLON
LINE
COOLING
WATER
PUMP
500-ml
CONDENSATE FLASKS
ICE WATER BATH
TENAX/
CHARCOAL
TRAP
SILICA
GEL
UMBILICAL
LINE
THERMOMETER
ROTAMETER
SHUT-OFF
VALVE
VACUUM
GAUGE
VENT
1ℓ/REV
DRY GAS
METER
CONTROL
VALVE
LEAK-FREE
PUMP
METER CONTROL UNIT

NOTE: CONDENSER/TRAP/FLASK JOINTS ARE IN TWO CONFIGURATIONS: ONE FOR NECKED-DOWN TUBE TRAPS AND ONE FOR SUSPENDED-TUBE TRAPS.

Figure 2-2. Schematic of single volatile organic sampling train (VOST).


GLASS CAP
VITON O-RING JOINT
C-CLIP
VITON O-RING BETWEEN TENAX TUBE O.D. AND TRAP I.D.
SCREEN
~5 in.
TENAX OR TENAX/CHARCOAL TUBE (10 cm x 1.6 cm GLASS) HOLDS APPROXIMATELY 2 grams SORBENT
120 mesh STAINLESS STEEL SCREEN
ZINC-COATED STEEL INTERNAL RETAINING RING ("C-CLIP")
VITON O-RING
VITON O-RING JOINT
GLASS CAP
TUBE LENGTH ~5 in.
TENAX OR TENAX/CHARCOAL TUBE (10 cm x 1.6 cm GLASS) HOLDS APPROXIMATELY 2 grams SORBENT
GLASS WOOL
1/4-in. SWAGELOK 316-SS NUT AND CAP (SUPELTEX M-1 FERRULES)

SUSPENDED-TUBE (ST)

NECKED-DOWN (ND)

Figure 2-3. Sorbent trap configurations.

The use of a quad train to collect duplicate samples of each sorbent trap configuration at the same time provided a better basis for statistically estimating and comparing the precision of each type of trap than would have been provided by collecting multiple samples with a single train at different times. The ability of the dilution system to reproduce desired test gas concentrations precisely was documented by results of the first five quad runs. Because this indicated that valid comparisons could indeed be made between samples collected at different times and because of the impracticality of trying to add equitable amounts of moisture to four trains at once, the moisture runs were made in pairs.

All sampling activities were conducted in a mobile laboratory separate from the analysis and sorbent preparation areas to prevent any cross-contamination from the different activities.

All sorbent traps were prepared from one lot of Tenax and one lot of charcoal to eliminate any bias in the results that might be caused by batch-to-batch differences in these reagents. In general, the sorbent traps were prepared and conditioned as specified in the protocol. As described later in Section 3, different conditioning procedures were used at different times. Sorbent raw materials were extracted and traps were packed near the beginning of the laboratory validation. The specific number of traps required for a given week's experiments were thermally conditioned during the preceding week so that the conditioning could be completed as close as possible to scheduled use. The thermal conditioning apparatus was set up to allow mass production of both trap configurations. Preparation and conditioning activities were performed in the Tenax preparation room, a separate area of the laboratory in which no solvents are handled or stored. The exact handling of each trap during preparation and conditioning activities was documented in a log book.

Each pair of traps was blank-checked as a unit following conditioning and prior to use. The blanking procedure consisted of thermally desorbing the traps, concentrating the blank sample cryogenically, flash-vaporizing the concentrated sample, and analyzing the sample by gas chromatography/flame ionization detection (GC/FID). The blank-checking apparatus was set up to permit handling of both types of trap designs with a minimum of changeover time. Traps were usually blank-checked during either the early part of the week in which they were used or the latter part of the preceding week. Because the GC/FID procedure gave only a general indication of blank levels, 1 out of 10 trap pairs was analyzed as a sample by gas chromatography/mass spectrometry (GC/MS) instead of GC/FID to determine actual blank levels of all the target compounds. Blank-checking activities were documented in a separate log book.

The sample storage conditions were the same for both trap configurations. Instead of storing prepared traps in ice water, we used the alternate procedure suggested in the protocol, which called for the traps to be placed in sealed metal cans containing charcoal and stored at ice temperature. After their final conditioning, all traps were stored in this manner until analysis.

All sorbent traps were analyzed in the same manner in general accordance with the protocol. Each trap was spiked with an internal standard and thermally desorbed with organic-free helium gas bubbled through organic-free water and trapped on an analytical sorbent trap. After the sample desorption steps, the analytical sorbent trap was rapidly heated and the carrier gas flow was reversed so that the effluent flow from the analytical trap was directed into the GC/MS. The volatile organics were separated by temperature-programmed gas chromatography and detected by low-resolution mass spectrometry. The mass of volatile compounds was calculated by the internal standard technique.

The VOST analytical apparatus was set up to allow analysis of either the ST or ND sample trap configuration by simply switching two three-way valves that connected the different thermal desorption devices for ST and ND traps in parallel.

Unless specifically designated otherwise, all samples were analyzed within one week of collection. Minimizing the time between blank checking and final analysis also minimized the potential for sample degradation.

The front (Tenax) and back (Tenax/charcoal) sorbent traps were analyzed separately for each sample run to determine in which portion of the train the target compounds were actually collected and to assess the potential for breakthrough.

2.4 EXPERIMENTS CONDUCTED

The experiments conducted during the laboratory validation included evaluating blanks, determining the precision and accuracy of the VOST protocol by use of a dry test gas, determining the effect of sample holding time, performing a ruggedness test, and determining the effect of moisture in the sample gas stream. These experiments are described briefly in the following subsections, and Table 2-2 presents a summary of testing activities and when they occurred.

2.4.1 Blank Evaluation

A series of sorbent traps was set aside and analyzed as blanks to determine the effectiveness of the sample preparation and conditioning measures,

TABLE 2-2. SUMMARY OF VOST LABORATORY VALIDATION TEST SCHEDULE

Week of laboratory study (Date 1984)	Type of experiment	Activities[a]
0 (April 23)	Preliminary blank evaluation	Analyzed 4 pairs of blank ST and 4 pairs of blank ND traps as samples; i.e., by GC/MS
1 (April 30)	Blank evaluation	Analyzed 4 pairs of blank ST and 4 pairs of blank ND traps as samples; i.e., by GC/MS
2 (May 7)	Precision and accuracy at 15 ppb, dry	Collected and analyzed 3 sets of quad samples (6 pairs ST and 6 pairs ND traps) plus blanks
	Sample preservation	Collected 2 sets of quad samples
3 (May 14)	Blank evaluation	Analyzed 2 pairs blank ST and 2 pairs blank ND traps as samples
4 (May 21)	Sample preservation	Analyzed 2 pairs each ST and ND traps collected during Week 2
	Ruggedness Test	Collected and analyzed 4 sets of paired runs at 15 ppb (half of ruggedness test) plus blanks
5 (May 28)	Blank evaluation	Analyzed remaining 2 pairs each type trap as samples
	Ruggedness Test	Collected and analyzed 4 sets of paired runs at 0.5 ppb (second half of ruggedness test) plus blanks
6 (June 4)	Precision and accuracy at 0.5 ppb, dry	Collected and analyzed 3 sets of quad samples plus blanks
7 (June 11)	Precision and accuracy at 15 ppb, ~30% moisture	Collected and analyzed 4 sets of paired runs plus blanks
	Sample preservation	Analyzed remaining 2 pairs each type of trap for samples collected during Week 2
8 (June 18)	Precision and accuracy at 0.5 ppb, ~30% moisture	Collected and analyzed 4 sets of paired runs plus blanks

[a] Conditioning, calibration, and pretest blank-checking activities were conducted throughout the test series.

and to see how the blank levels changed with time. The VOST protocol specifies that the conditioned traps be stored until ready for field use, but it does not specify the time period between conditioning and use. Results of the blank evaluation were expected to provide some guidance on time limits and to determine any difference between the ST and ND designs.

A batch of each trap type was conditioned and stored at ice temperature (~4°C) in metal cans containing charcoal until they were analyzed by GC/MS to determine blank values. Initially, a set of preliminary blank evaluation samples was analyzed to check the effectiveness of conditioning. The preliminary set consisted of two pairs (a pair consisted of one Tenax and one Tenax/-charcoal trap) of each trap configuration (ND and ST). The blank evaluation sample set consisted of six additional pairs of each trap type, which were analyzed as follows: two pairs each of ND and ST traps initially, two pairs each two weeks later, and each of the remaining two pairs two weeks after that, or a total of four weeks later than the initial pairs. Differences between ND and ST types, Tenax and Tenax/charcoal traps, and holding times of 0, 2, and 4 weeks were investigated.

2.4.2 Precision and Accuracy Determinations Using A Dry Test Gas

A series of quad sample runs was conducted to determine VOST precision and accuracy and to compare ND and ST trap types. These tests were run under generally optimum conditions to obtain the best possible results and to minimize the potential effects of interferences. This approach would allow the results of subsequent tests designed specifically to determine the effects of potential interferences to be compared with optimum results and make it easier to differentiate any effects. These baseline tests involved three quad runs (Q1, Q2, and Q3) at a nominal target compound concentration of 15 ppb. Later, three additional quad runs (Q6, Q7, and Q8) were made at a nominal target compound concentration of 0.5 ppb. The test gas for all these runs consisted of the target compounds in dry air, and the samples were collected at nominal VOST protocol sampling conditions (a sampling rate of 1 liter per minute and a sampling volume of 20 liters).

2.4.3 Sample Holding Time

The protocol specifies that sample traps be stored at 4°C until analysis, but it does not give any guidance on how long the samples could be stored without impairing results. Two sets of quad samples (Q4 and Q5) were collected at the same conditions as samples from Runs Q1 through Q3 and set aside for analysis at different time intervals for comparison with results of Runs Q1 through Q3. Each set of quad samples consisted of two pairs of ST traps and two pairs of ND traps. Samples from Run Q4 were analyzed 2 weeks later than those from Q1 through Q3, and Run Q5 samples were analyzed 5 weeks later than the Q1 through Q3 samples. A 5-week interval was used instead of 4 weeks to accommodate the overall analytical schedule. Differences between trap types were evaluated, as well as holding times.

2.4.4 Ruggedness Tests

A series of tests was conducted to determine if changes in any of several selected variables had a significant impact on results obtained by the VOST method, and if so, which should be selected for further evaluation. The procedures outlined in Youden's Ruggedness Tests* were used as guidelines. The procedures and results are described in Appendix E.

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*Statistical Manual of the Association of Official Analytical Chemists, Youden and Steiner, 1975.

2.4.5 Precision and Accuracy Determinations Using A Moisture-Laden Test Gas

The original intent was to use the results of the ruggedness tests to determine whether further evaluation of the selected variables was necessary. If no further evaluation of these variables was necessary, several repeat test runs on a dry test gas at 0.5 and 15 ppb would be conducted to determine if experience gained with the quad VOST system had any effect on observed precision and accuracy.

Four paired runs (Runs W1 through W4) were conducted at nominal test gas conditions of 15 ppb of each target compound and approximately 30 percent moisture by volume. Each paired run consisted of two identical trains, either ND or ST type, operated at nominal VOST sampling conditions. Four additional runs (W5 through W8) were conducted in a similar manner, but the level of target compounds was 0.5 ppb each. Results of these "wet" tests were evaluated for differences between train types and compared against the results of the "dry" tests to determine if moisture had any effect on observed results.

2.5 ANALYSIS OF RESULTS

Results for each sample run and target compound were calculated in nanograms per liter of gas sampled (ng/liter). The relative standard deviation (RSD) for each pair of duplicate trains was determined for use in estimating precision. Statistical models were developed to perform an analysis of variance (ANOVA) and t-test by computer program. The ANOVA and t-test calculations were performed on data from the experiments just described (except the ruggedness tests) to determine if the measured results of the ND and ST trap configurations showed any statistically significant differences.

The results of the ruggedness tests were analyzed according to the procedures outlined by Youden. Because the target compound concentration was one of the designated variables, measured concentrations were normalized to the expected values to avoid the interpretations of effects being biased by the high concentrations. The normalized results from each sample run were combined in different formulas so that the response due to each level of each variable could be determined by cancelling the effects of the other variables. Youden's procedure is explained in more detail in Appendix E, which also presents the results.

SECTION 3

EXPERIMENTAL PROCEDURES

This section describes in detail the equipment and procedures used during the laboratory evaluation and discusses how they differ from those specified in the VOST protocol. Included in the discussions are the dilution system, sampling trains, sorbent trap preparation and conditioning, pretest blank checking, GC/MS analysis, and GC/MS calibration as well as appropriate quality assurance measures.

3.1 TEST GAS DILUTION SYSTEM

Figure 3-1 is a schematic of the equipment used to generate dry test gases containing target compounds at two nominal levels, 15 and 0.5 ppb. The dilution system was operated in the same manner for "wet" runs and for "dry" runs; for the wet runs, moisture was added to the test gas between the manifold and sample lines.

Teflon tubing was used to connect gases from the three cylinders to the dilution system module. A filter cartridge containing molesieve and activated charcoal was placed in the air line to remove trace levels of organic compounds. Gas flow rates of individual cylinders were set with stainless steel metering valves and monitored with glass rotameters. The rotameter tubes and floats for the target compounds differed for tests at 15 and 0.5 ppb because different dilution ratios were required. The changeover was relatively easy, as the nominal test gas concentration was not changed within

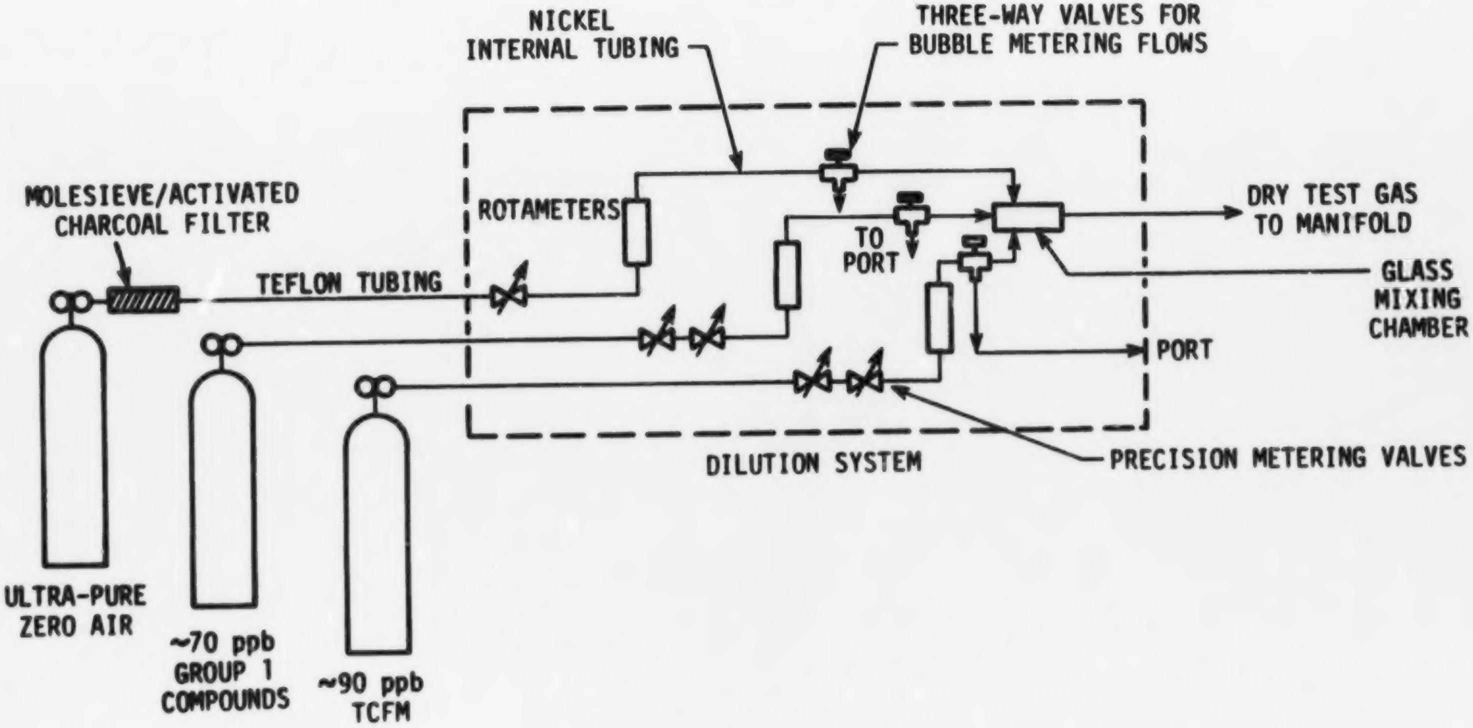

NICKEL INTERNAL TUBING
THREE-WAY VALVES FOR BUBBLE METERING FLOWS
MOLESIEVE/ACTIVATED CHARCOAL FILTER
ROTAMETERS
TEFLON TUBING
TO PORT
DRY TEST GAS TO MANIFOLD
GLASS MIXING CHAMBER
PORT
DILUTION SYSTEM
PRECISION METERING VALVES
ULTRA-PURE ZERO AIR
~70 ppb GROUP 1 COMPOUNDS
~90 ppb TCFM

Figure 3-1. Test gas dilution system.

a given week. The glass tubes and floats were cleaned with soap and water between changes. Individual gas flow rates were fine-tuned and checked by in-line, three-way, stainless steel valves and a calibrated bubble meter. When the desired gas flows were achieved, the three gas streams were routed to a glass mixing chamber and then to the outlet port of the dilution system. A length of Teflon tubing (approximately 1.5 meters) was used to transport the test gas to the four-port Teflon manifold. Excess gas from the manifold was vented through larger-diameter tubing to a hood. Approximately 30 minutes prior to a sample run, the three cylinder gas flows were rechecked by bubble meter two or more times to obtain accurate flow measurements and dilution ratios. After a sample run, the three gas flows were rechecked at least once with a bubble meter to assure stability over the duration of the run.

The dilution system operated flawlessly during the laboratory evaluation tests. Table 3-1 presents a summary of the dilution system data and the expected concentrations of the target compounds based on the dilution system flows and gas cylinder concentrations. The gas flow rates shown for each run are based on the average of pre- and post-run bubble meter measurements. Flows were very stable, and the difference in flow measurements over a given run was no greater than the differences between runs. Expected concentrations of the target compounds are shown in parts per billion and nanograms per liter for each run. The mean concentration, standard deviation, and relative standard deviation (percentage) are shown to demonstrate the comparability of expected concentrations for each group of similar runs. Runs Q1 through Q5 were conducted at similar test gas conditions. As indicated, the relative standard deviation was less than 0.5 percent for any one compound

TABLE 3-1. SUMMARY OF DILUTION SYSTEM DATA AND EXPECTED SPECIES CONCENTRATION FOR PRECISION AND ACCURACY TESTS

Date (1984)	Run No.	Average dilution system flow rates, liters/min			Expected species concentrations at manifold											
					Vinyl chloride		Trichloro-fluoromethane		Chloroform		Carbon tetrachloride		Benzene		Tetra-chloroethylene	
		Group 1 cylinder[a]	TCFM cylinder[b]	Total to manifold[c]	ppb	ng/liter	ppb	ng/liter	ppb	ng/liter	ppb	ng/liter	ppb	ng/liter	ppb	ng/liter
5/9	Q1	1.364	0.985	5.963	16.36	42.52	14.83	84.84	13.86	68.85	15.05	96.29	15.19	49.34	15.65	108.0
5/9	Q2	1.369	0.977	5.960	16.42	42.70	14.72	84.20	13.92	69.14	15.11	96.70	15.25	49.55	15.71	108.4
5/9	Q3	1.371	0.982	5.972	16.41	42.67	14.77	84.46	13.91	69.10	15.10	96.64	15.24	49.52	15.24	108.4
5/11	Q4	1.380	0.989	6.059	16.28	42.34	14.66	83.84	13.80	68.55	14.99	95.88	15.12	49.13	15.58	107.5
5/11	Q5	1.377	0.986	6.035	16.31	42.41	14.67	83.92	13.83	68.68	15.01	96.05	15.15	49.22	15.61	107.7
Combined statistics		x̄, ng/liter σ, ng/liter %, RSD				42.53 0.157 0.37		84.25 0.410 0.49		68.86 0.257 0.37		96.31 0.358 0.37		49.35 0.183 0.37		108.0 0.406 0.38
6/5	Q6	0.045	0.033	5.991	0.54	1.40	0.49	2.83	0.46	2.26	0.49	3.16	0.50	1.62	0.51	3.54
6/5	Q7	0.046	0.033	6.011	0.55	1.42	0.49	2.82	0.46	2.30	0.50	3.22	0.51	1.65	0.52	3.61
6/6	Q8	0.046	0.034	5.993	0.55	1.43	0.51	2.91	0.46	2.31	0.50	3.23	0.51	1.66	0.52	3.62
Combined statistics		x̄, ng/liter σ, ng/liter %, RSD				1.42 0.015 1.0		2.85 0.049 1.7		2.29 0.026 1.1		3.20 0.038 1.2		1.64 0.021 1.3		3.59 0.044 1.2
6/12	W1	1.362	1.001	5.982	16.28	42.32	15.03	85.95	13.80	68.53	14.98	95.85	15.12	49.12	15.57	107.5
6/12	W2	1.370	1.001	5.967	16.42	42.68	15.06	86.16	13.91	69.10	15.11	96.65	15.24	49.53	15.70	108.4
6/13	W3	1.358	0.998	5.951	16.32	42.42	15.06	86.14	13.83	68.68	15.02	96.06	15.15	49.22	15.61	107.7
6/13	W4	1.358	1.000	5.929	16.38	42.58	15.14	86.63	13.88	68.94	15.07	96.42	15.21	49.41	15.67	108.1
Combined statistics		x̄, ng/liter σ, ng/liter %, RSD				42.50 0.161 0.38		86.22 0.289 0.34		68.81 0.256 0.38		96.24 0.358 0.37		49.32 0.184 0.37		107.9 0.403 0.37
% Difference, W_1^4 vs Q_1^5[d]						-0.07		2.34		-0.07		-0.07		-0.06		-0.09

(continued)

TABLE 3-1 (continued)

Date (1984)	Run No.	Average dilution system flow rates, liters/min			Expected species concentrations at manifold											
					Vinyl chloride		Trichlorofluoromethane		Chloroform		Carbon tetrachloride		Benzene		Tetrachloroethylene	
		Group 1 cylinder[a]	TCFM cylinder[b]	Total to manifold[c]	ppb	ng/liter	ppb	ng/liter	ppb	ng/liter	ppb	ng/liter	ppb	ng/liter	ppb	ng/liter
6/19	W5	0.045	0.033	5.960	0.54	1.40	0.49	2.84	0.46	2.27	0.50	3.18	0.50	1.63	0.52	3.56
6/19	W6	0.045	0.033	6.019	0.53	1.39	0.49	2.82	0.45	2.25	0.49	3.15	0.50	1.61	0.51	3.53
6/19	W7	0.045	0.033	5.990	0.54	1.40	0.49	2.83	0.46	2.26	0.49	3.16	0.50	1.62	0.51	3.55
6/20	W8	0.045	0.033	5.960	0.54	1.40	0.49	2.84	0.46	2.27	0.50	3.18	0.50	1.63	0.52	3.56
Combined statistics	$\bar{x}$, ng/liter σ, ng/liter %, RSD					1.40 0.005 0.35		2.83 0.010 0.35		2.26 0.010 0.44		3.17 0.015 0.47		1.62 0.010 0.62		3.55 0.014 0.39
% Difference, W_1^5 vs Q_6^8[d]						-1.41		-0.70		-1.31		-0.94		-1.22		-1.11

[a] Undiluted cylinder concentrations used to calculate expected values are 71.5 ppb vinyl chloride; 60.6 ppb chloroform; 65.8 ppb carbon tetrachloride; 66.4 ppb benzene; and 68.4 ppb tetrachloroethylene in nitrogen.

[b] Undiluted cylinder concentration used to calculate expected values is 89.8 ppb trichlorofluoromethane in nitrogen.

[c] Includes dilution air cylinder gas flow, which is not shown, and both cylinders of known gases.

[d] % Difference = $\frac{\bar{W}_1^n - \bar{Q}_1^n}{\bar{Q}_1^n}$ x 100.

over these five runs. Runs Q6 through Q8 were conducted at a nominal concentration of 0.5 ppb. The relative standard deviation for any one compound over these three runs was no more than 1.7 percent. Results for the other two groups of similar runs were comparable.

Table 3-1 also shows the differences in mean expected concentrations between groups of "dry" and "wet" runs conducted at the same nominal test gas concentration. This difference (shown as a percentage) indicates the reproducibility of expected concentrations from one week to another and demonstrates the degree of error associated with comparing results of tests conducted during different weeks. Results show that the difference in mean concentration between Runs Q1 through Q5 and Runs W1 through W5 (≈15 ppb) was less than 2.5 percent. The comparison between runs at 0.5 ppb was even better. (Results for the ruggedness tests were similar and are reported in Appendix E.)

Several quality assurance checks were made in regard to the dilution system and cylinder gases. Before any sample runs were made, the dilution system module was leak-checked by pressurizing the sealed unit to 35 psig. No change in pressure was observed over a 15-minute period. The dilution system was checked independently for accuracy and stability by the use of stable sulfur dioxide (SO_2) cylinder gases and an SO_2 continuous gas analyzer. The stability was demonstrated to be within ±0.5 percent over a 6-hour period. The relative accuracy was -6 percent, based on comparison of measured and expected SO_2 concentrations. These checks were made at dilution settings representative of those used to generate 0.5-ppb test gases, or worst-case conditions. The dilution error value includes an approximately ±3 percent error in the SO_2 measurement system.

A blank check of the dilution system was also made. One of the zero air cylinders to be used in the study was connected to the dilution system with an in-line filter cartridge containing molesieve and activated charcoal. Two nitrogen (N_2) cylinders were connected to the system with the same regulators that were used with the Group 1 and TCFM cylinders. The dilution system was then purged with the N_2 and air cylinder gases at a typical dilution ratio. Approximately 20 liters of the effluent gas was loaded onto a Tenax trap to simulate an actual VOST sample and analyzed by GC/MS. Blank levels of the six target compounds were no higher than in the Tenax itself. All of the these results were considered acceptable.

Three different cylinders of ultra-pure air (total hydrocarbon content less than 0.1 ppm) were used over the duration of the project. Activated charcoal in the filter cartridge was freshened with each cylinder change to ensure purity of the dilution gas.

One cylinder of TCFM and one cylinder of Group 1 compounds were used throughout the study. Research Triangle Institute (EPA's designated holder of audit materials) analyzed the Group 1 cylinder prior to and after the laboratory study to verify the labeled cylinder values and stability. Because time did not permit verification of the content of the TCFM cylinder prior to the study, the manufacturer's value was used; however, RTI did analyze the TCFM cylinder after the tests were completed. All of RTI's results were within ±10 percent of the initial cylinder values; therefore, the initial values were used in all calculations of expected concentrations.

3.2 SAMPLING SYSTEMS

A quad VOST was used to collect four samples simultaneously from a manifold purged with dry test gas. Each sample represented a pair of sorbent traps: a Tenax trap connected in series with a Tenax/charcoal trap. Two configurations of sorbent trap design were used. Sampling equipment and procedures are presented first for the dry test gas conditions. Variations used for the wet tests and ruggedness tests are presented later.

3.2.1 Sampling Equipment and Sorbent Trap Design

The quad VOST has a common probe, probe purge system, and digital temperature indicator. Except for these, each of the four trains has its own components. Figure 3-2 is a schematic of the quad probe and sample box. Figure 3-3 is a schematic of an individual sampling train.

Probe--

A stainless steel sheath and four ¼-in.-o.d. Teflon tube liners (with a common heating system capable of maintaining a gas temperature of at least 130°C at the exit end) was used. The four probe liners were connected separately at one end to the test gas manifold and to the individual four-way valves of each sampling train at the other. Two thermocouples were used to monitor probe temperature: one inside the four-tube probe bundle and one on the outer edge of the bundle. Both thermocouples were located near the middle of the probe. Figure 3-4 is a schematic of the quad VOST probe.

Four-Way Valves--

A Teflon four-way valve was used to connect each sampling train to either the probe or the leak-check system and the probe to either the sampling train or the purge system. In the leak-check/probe-purge position, the probe was connected to the purge system and the train was connected to the leak-check system; in the sample position, the probe was connected to the train and the purge system was connected to the leak-check system. The use

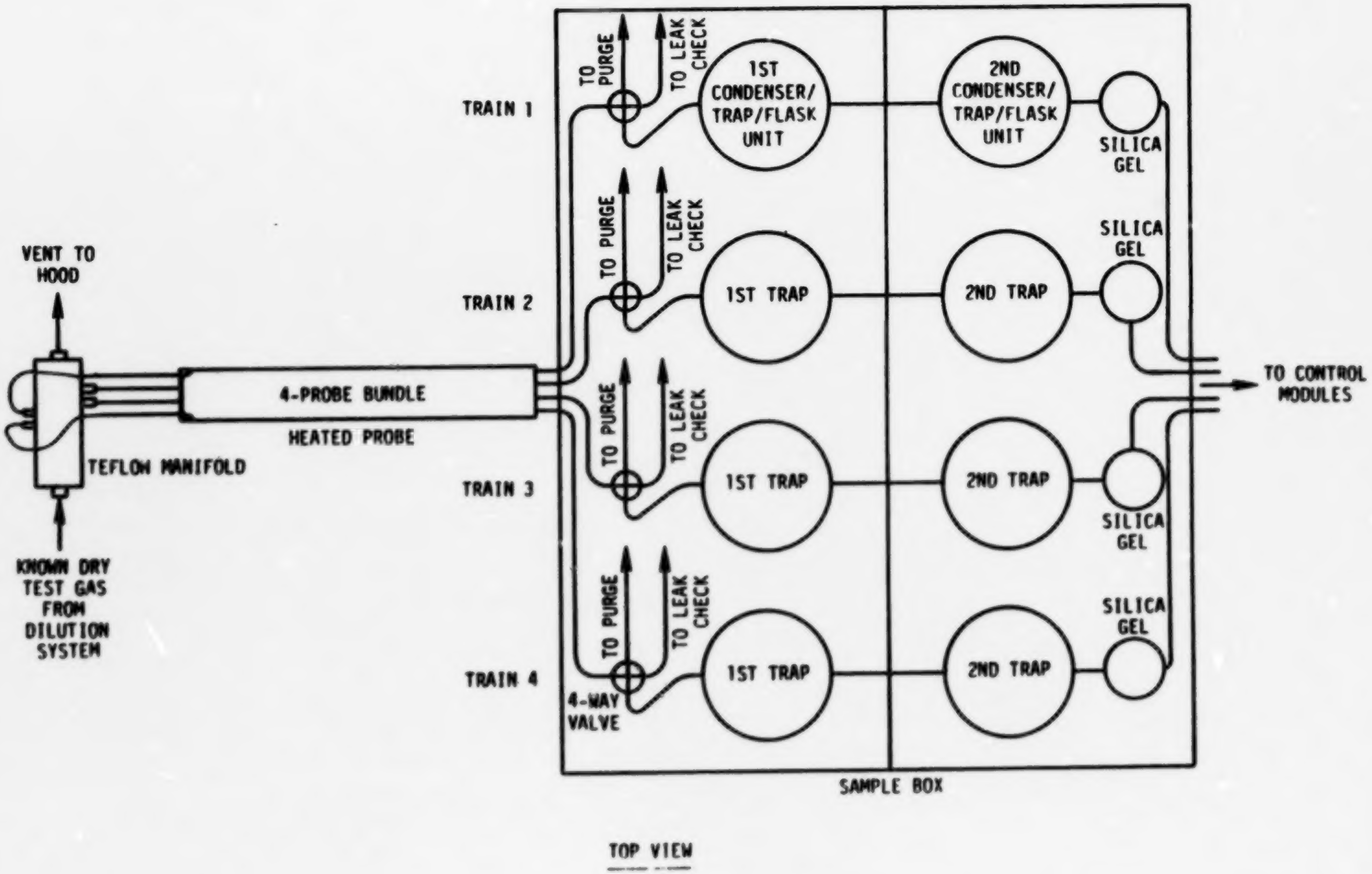
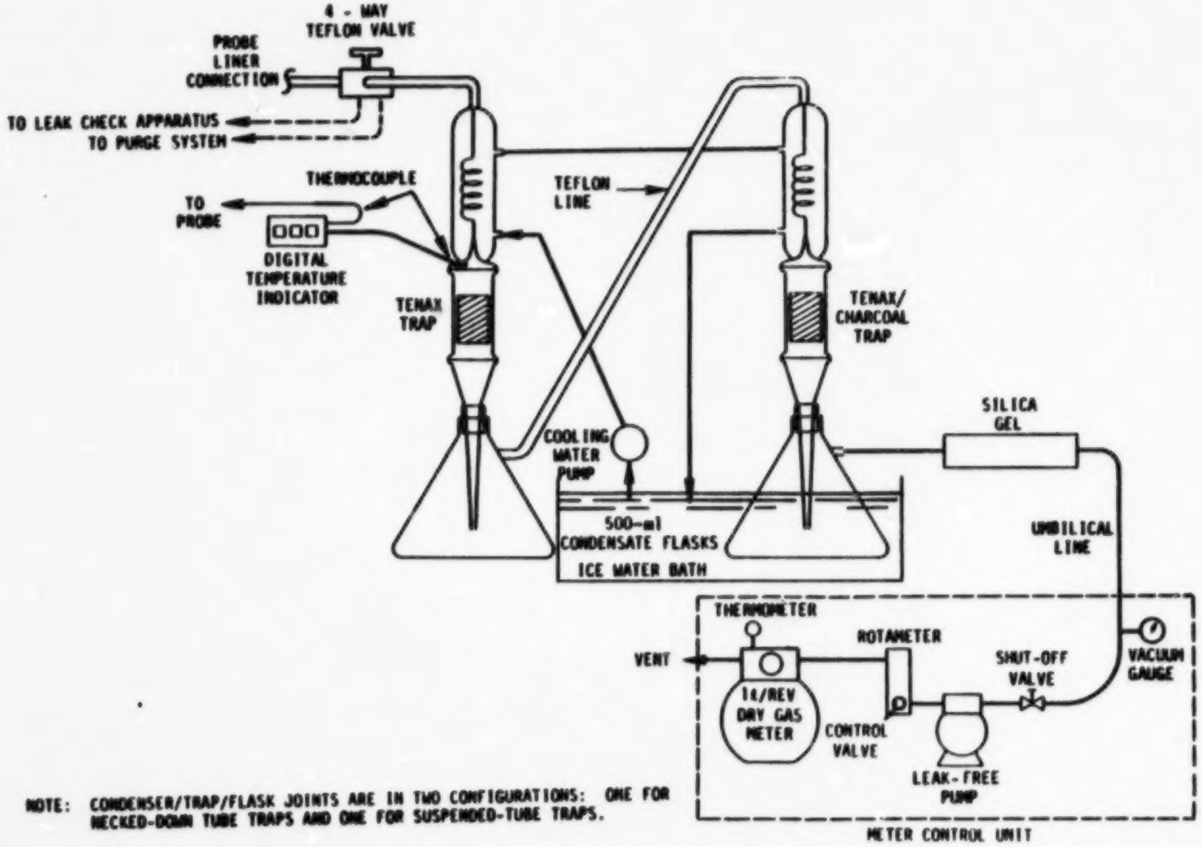

TRAIN 1
TRAIN 2
TRAIN 3
TRAIN 4
TO PURGE
TO LEAK CHECK
1ST CONDENSER/ TRAP/FLASK UNIT
2ND CONDENSER/ TRAP/FLASK UNIT
1ST TRAP
2ND TRAP
SILICA GEL
4-WAY VALVE
SAMPLE BOX
TO CONTROL MODULES
VENT TO HOOD
4-PROBE BUNDLE
HEATED PROBE
TEFLON MANIFOLD
KNOWN DRY TEST GAS FROM DILUTION SYSTEM
TOP VIEW

Figure 3-2. Simplified schematic of quad VOST.



4 - WAY TEFLON VALVE
PROBE LINER CONNECTION
TO LEAK CHECK APPARATUS
TO PURGE SYSTEM
THERMOCOUPLE
TO PROBE
DIGITAL TEMPERATURE INDICATOR
TENAX TRAP
TEFLON LINE
TENAX/CHARCOAL TRAP
COOLING WATER PUMP
500-ml CONDENSATE FLASKS
ICE WATER BATH
SILICA GEL
UMBILICAL LINE
THERMOMETER
VENT
1ℓ/REV DRY GAS METER
ROTAMETER
CONTROL VALVE
LEAK-FREE PUMP
SHUT-OFF VALVE
VACUUM GAUGE
METER CONTROL UNIT

NOTE: CONDENSER/TRAP/FLASK JOINTS ARE IN TWO CONFIGURATIONS: ONE FOR NECKED-DOWN TUBE TRAPS AND ONE FOR SUSPENDED-TUBE TRAPS.

Figure 3-3. Schematic of single volatile organic sampling train (VOST).

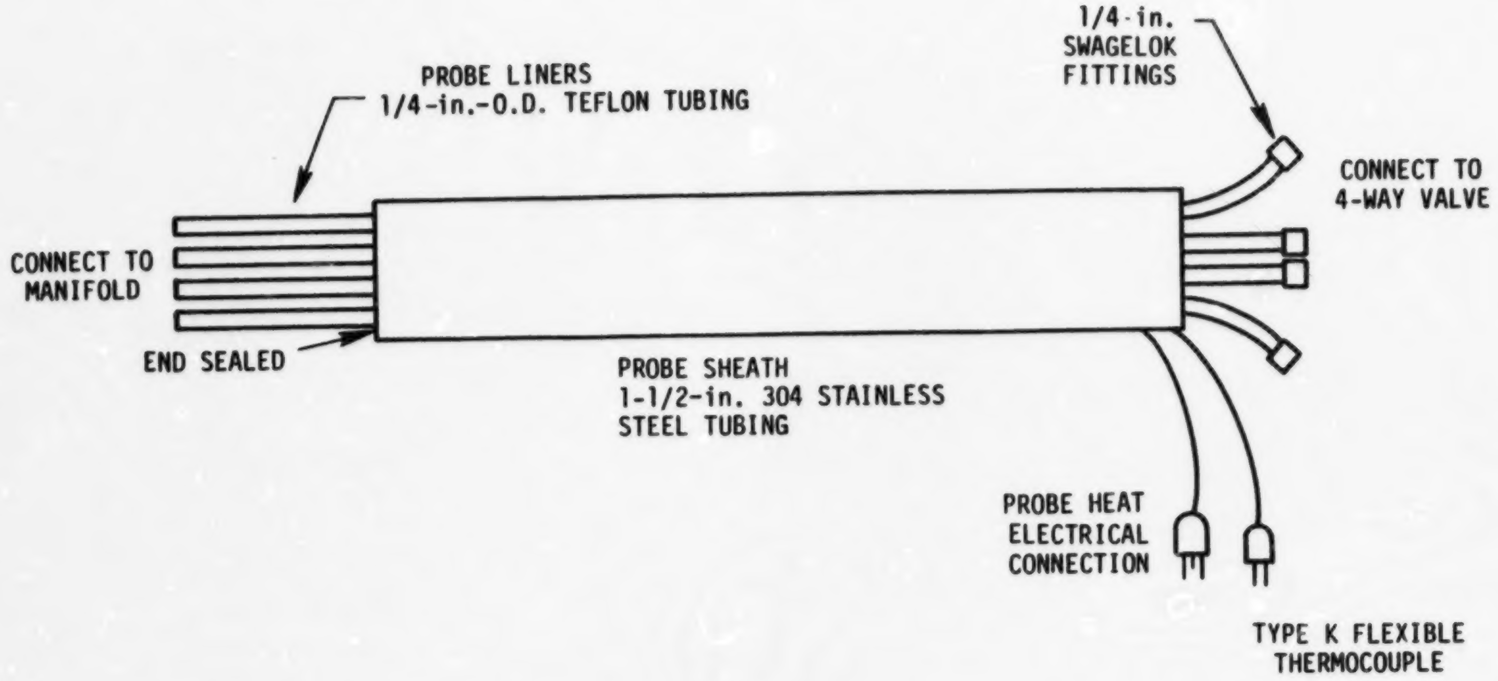

PROBE LINERS
1/4-in.-O.D. TEFLON TUBING
1/4-in.
SWAGELOK
FITTINGS
CONNECT TO
4-WAY VALVE
CONNECT TO
MANIFOLD
END SEALED
PROBE SHEATH
1-1/2-in. 304 STAINLESS
STEEL TUBING
PROBE HEAT
ELECTRICAL
CONNECTION
TYPE K FLEXIBLE
THERMOCOUPLE

Figure 3-4. Quad VOST probe details.

of one four-way valve instead of several two- or three-way valves, as specified in the protocol, should not have affected results. If a good leak-check can be obtained, either valve arrangement should be acceptable.

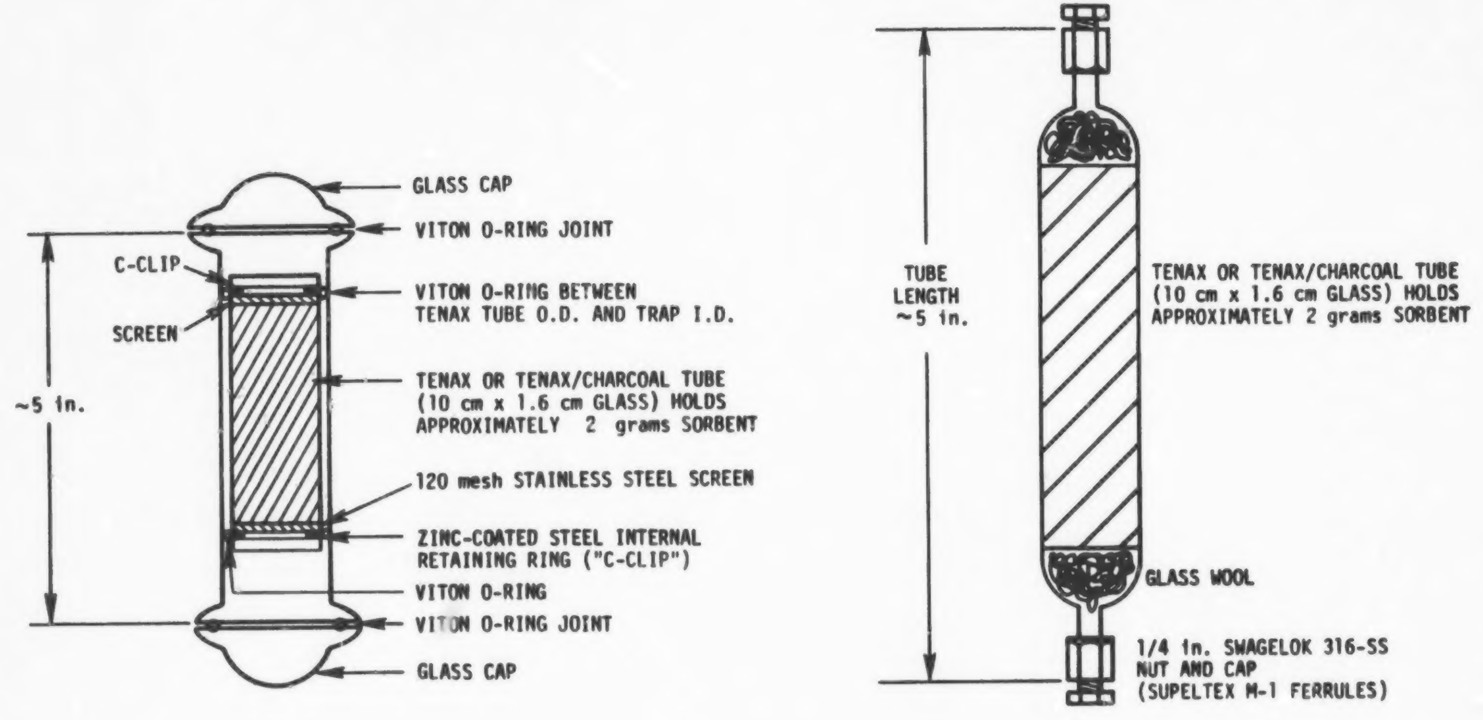
Condensers--

Glass coil condensers with water jackets were used to cool the sample gas stream to 20°C or less before it entered the first sorbent trap. A 7-cm length of Teflon tubing and a Teflon union were used to connect the inlet of each condenser to each four-way valve. A thermocouple attached to the outlet of the first condenser was used to monitor the temperature of the gas entering the first trap. A second condenser was used between the two sorbent traps, and a submersible pump recirculated ice water between the bath and condensers.

Sorbent Traps--

Each train contained two traps in series. The first trap contained 1.6 g of Tenax and the second one contained approximately 1 g each of Tenax and charcoal. The second trap was oriented such that the sample gas passed through the Tenax portion before the charcoal. Traps were prepared by the procedures outlined later in Subsection 3.3.

Both types of sorbent trap configurations in the VOST protocol were evaluated to ascertain any statistically significant difference between the two. Figure 3-5 depicts the necked-down (ND) trap design and PEI's version of the suspended-tube (ST) trap design. The ST design is referred to as the inside/outside (I/O) configuration in the VOST protocol. Although PEI's ST design and the protocol ST design are based on the same principle, there are minor differences. Basically, the protocol ST design incorporates an O-ring


GLASS CAP
VITON O-RING JOINT
C-CLIP
SCREEN
VITON O-RING BETWEEN TENAX TUBE O.D. AND TRAP I.D.
~5 in.
TENAX OR TENAX/CHARCOAL TUBE (10 cm x 1.6 cm GLASS) HOLDS APPROXIMATELY 2 grams SORBENT
120 mesh STAINLESS STEEL SCREEN
ZINC-COATED STEEL INTERNAL RETAINING RING ("C-CLIP")
VITON O-RING
VITON O-RING JOINT
GLASS CAP
TUBE LENGTH ~5 in.
TENAX OR TENAX/CHARCOAL TUBE (10 cm x 1.6 cm GLASS) HOLDS APPROXIMATELY 2 grams SORBENT
GLASS WOOL
1/4 in. SWAGELOK 316-SS NUT AND CAP (SUPELTEX M-1 FERRULES)

SUSPENDED TUBE (ST)

NECKED-DOWN (ND)

Figure 3-5. Sorbent trap configurations.

seal of the protective outer glass wall against grooved steel plates at each end. Swagelok tube fittings affixed to the plates are used to connect the assembled traps to the sampling train. In PEI's version of this design, the O-ring seal of the protective outer wall also serves as the connection joint to the sampling train. Otherwise, both designs are essentially identical.

The ND design is referred to in the protocol as the inside/inside (I/I) configuration. The trend in volatile organic sampling is toward the use of this design because it is easy to handle. Also, because the desorption purge gas does not contact the outside of the Tenax trap during analysis, the potential for contamination is less than with the ST design. During analysis of the ST samples, the entire Tenax trap that is suspended within the protective center wall is exposed to desorption purge gas. Condensers and flasks were made with both ST and ND types of joint connections.

Condensate Flasks--

Each train had a 500-ml impinger-type glass flask connected to the outlet of each sorbent trap. Teflon tape was used in the ground-glass joints of the two-piece flasks to eliminate leaks. The impinger stems were all approximately 13 mm from the flask bottoms.

The use of 500-ml condensate flasks instead of the 125-ml flasks specified in the protocol should not have affected laboratory validation results. The VOST protocol does not contain a specification for the impinger stem; i.e., whether the stem should be cut short to avoid gas bubbling through any collected condensate, or whether it should be close to the flask bottom so that bubbling can occur. Because of the low potential amount of condensate (approximately 15 ml per 20-liter sample at 50 percent moisture), this may be a moot question in most cases, especially for this laboratory study. Nevertheless, a definitive approach for handling any aqueous condensate should be specified in protocol revisions. For this laboratory study, aqueous condensate collected during wet runs was recovered after each run. Selected condensate samples were subsequently analyzed.

Another difference from the protocol is the use of a flask between the second sorbent trap and the silica gel container. The use of this flask was discontinued in the current VOST protocol because experience indicated no condensate was being collected in it. Whether or not this flask is used should be of no significance.

Drying Tube--

Teflon containers holding approximately 100 g of silica gel were used to remove residual moisture from the sample gas stream prior to its entering the metering system.

Metering System--

The metering system consisted of an umbilicial line, vacuum gauges, leak-free diaphragm pump, a calibrated rotameter, and a Singer dry-gas meter that measured 1 liter/revolution with 2 percent accuracy for flow rates between 0.5 and 1.0 liter/min.

Connecting Lines--

All sample transfer lines between the first trap and silica gel container were Teflon and were attached to glassware with Teflon fittings. The NDT traps were connected with 316 stainless steel fittings with Supeltex M-1 ferrules. The ST traps were connected with Viton O-rings. Leak-free connections were made without the use of sealing grease.

Leak-Check System--

A Teflon container filled with approximately 50 g of activated charcoal, a shutoff valve, and Teflon tubing were connected to each four-way valve to filter ambient air when the vacuum was released in the sampling train after leak checks. A sketch of the leak-check apparatus is shown in Figure 3-6. The charcoal containers were packed initially and were not changed during the study.

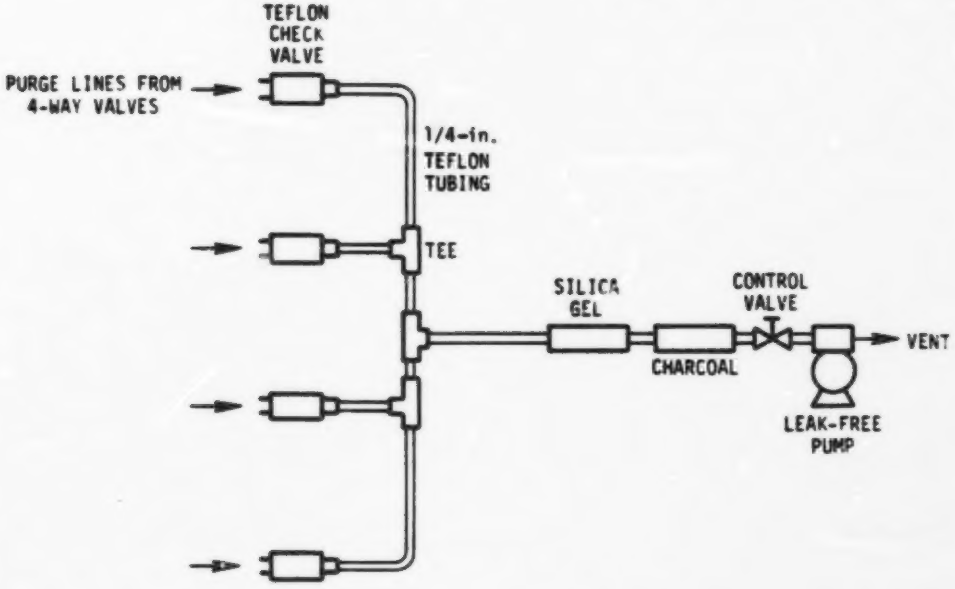
Probe Purge System--

A diaphragm pump, tubing, and related equipment were used to purge test gas through the probe and all four train valves simultaneously. A check valve was located in each line to prevent reverse flow of ambient air into the leak-check system when the four-way valve was in the sampling position. A sketch of the purge system is also shown in Figure 3-6.

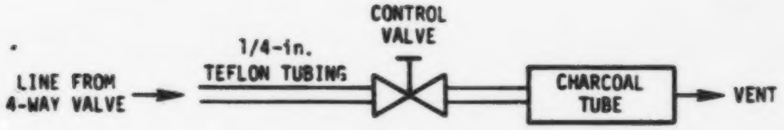
All reagents and equipment were cleaned and prepared by procedures described in Subsection 3.3; however, the probe liners were made from new tubing so no cleaning was necessary. Pre- and post-test calibration data for the sampling equipment are summarized in Section 5.

3.2.2 Dry Test Gas System

For Runs Q1 through Q8, the quad VOST and gas dilution system were set up as shown in Figure 3-7. The setup of the individual trains was as shown earlier in Figure 3-3. The silica gel containers were packed initially and were not changed during the study. Each quad run consisted of two ND trains


TEFLON CHECK VALVE
PURGE LINES FROM 4-WAY VALVES
1/4-in. TEFLON TUBING
TEE
SILICA GEL
CONTROL VALVE
VENT
CHARCOAL
LEAK-FREE PUMP

PURGE SYSTEM


CONTROL VALVE
1/4-in. TEFLON TUBING
LINE FROM 4-WAY VALVE
CHARCOAL TUBE
VENT

LEAK CHECK SYSTEM (ONE OF FOUR)

Figure 3-6. Leak-check and probe-purge systems for quad VOST.

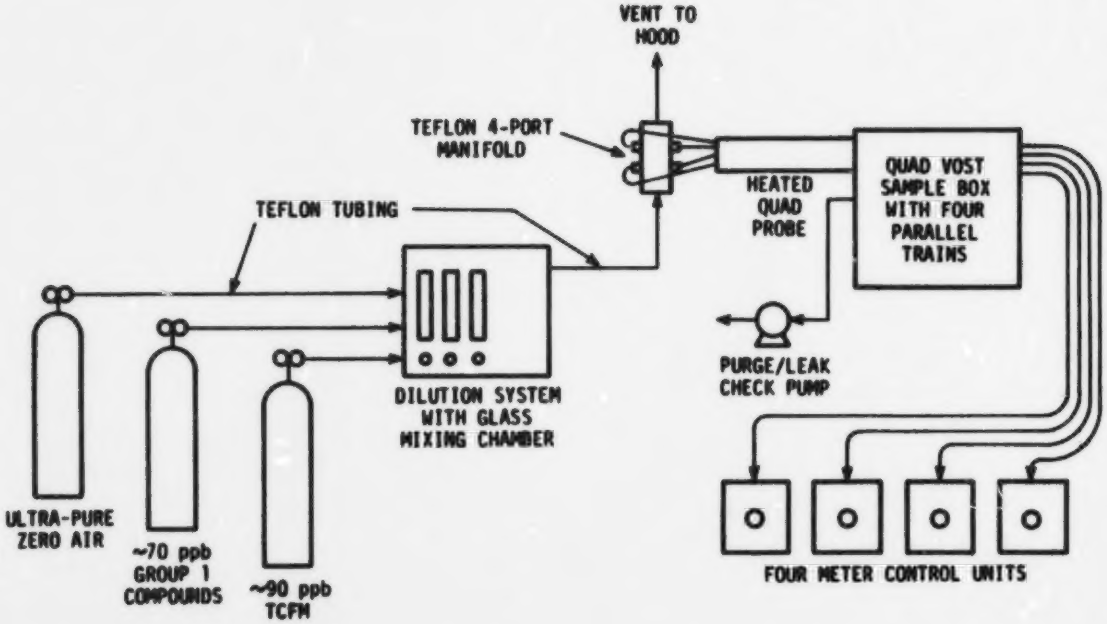

VENT TO HOOD
TEFLON 4-PORT MANIFOLD
TEFLON TUBING
HEATED QUAD PROBE
QUAD VOST SAMPLE BOX WITH FOUR PARALLEL TRAINS
PURGE/LEAK CHECK PUMP
DILUTION SYSTEM WITH GLASS MIXING CHAMBER
ULTRA-PURE ZERO AIR
~70 ppb GROUP 1 COMPOUNDS
~90 ppb TCFM
FOUR METER CONTROL UNITS

Figure 3-7. Schematic of sampling arrangement for dry test gas system.

and two ST trains. The positions of each glassware set, probe line, and meter control units were rotated between runs to eliminate inherent biases.

A leak check of the probe system was conducted at the beginning of each test day and again after any assembly changes to that portion of the train. With the four-way valve in the leak-check/probe-purge setting, a leak-check device consisting of a vacuum gauge, a shutoff valve, and a charcoal tube was connected to the probes. With the shutoff valve in the closed position, the purge pump was turned on, and a vacuum of 250 mmHg was pulled on the system. The probe was isolated from the purge pump and the leak rate noted. The acceptance criterion for the leak check was that no discernible leakage be present (i.e., a leakage rate of less than 2.5 mmHg/min). If the leak check did not meet this criterion, the problem was identified, corrected, and the leak check was repeated. At the completion of each leak check, the probe system was returned to ambient pressure by opening the shutoff valve and allowing charcoal-filtered ambient air to pass through the system.

Each train was leak-checked by turning the four-way valve to the leak-check/probe-purge setting, closing the leak-check valve at the charcoal container, and pulling a 250-mmHg vacuum. The traps and condensers were isolated from the pump by closing the shutoff valve in the control module, and the leak rate was noted. The acceptance criterion for the pretest leak check was that no discernible leakage be present (i.e., a leakage rate of less than 2.5 mmHg/min). If the leak check did not meet these specifications, the problem was identified, corrected, and the leak check was repeated. At the completion of each leak check, the train was returned to ambient pressure by opening the leak-check valve and allowing charcoal-filtered ambient air to pass through the train.

At the completion of all train leak checks, the dry test gases were allowed to pass through the dilution system and purge the manifold until steady-state conditions were reached. The flow rate of each gas stream at the dilution system was calibrated with a bubble meter. When the flow rates of all of the gas streams were set, the manifold was purged for a minimum of 5 minutes. The flow rate of test gas to the manifold was approximately 50 percent more than the total required by the sampling trains. At the completion of the manifold purge, the sampling train purge pump was turned on, and the probes were purged with the test gases for a minimum of 10 minutes. The total purge rate for all four probe liners was approximately 2.5 to 3 liters per minute, which was less than the total flow to the manifold. Meanwhile, all temperature settings were checked for proper readings, water was circulated through the coil condensers, ice was added to the coolant bath, and dry gas meters were reset to zero.

At the completion of the probe purge, the four-way valve on each train was switched from the leak-check/purge setting to the sample setting. The sample runs were started sequentially by turning on the pump and setting the required sampling rate by means of a calibrated rotameter. All of the dry test gas runs were conducted at a sampling rate of 1 liter/min and a volume of 20 liters.

Sample time, meter volume, rotameter setting, meter temperature, primary condenser exit temperature, probe temperatures, and vacuum readings were recorded at 5- or 10-minute intervals. Adjustments were made as necessary to maintain the desired flow rate, a probe temperature greater than 130°C, and a primary condenser exit temperature less than 20°C. Sampling was continued until the desired 20-liter sample volume was attained. As each run was concluded, the four-way valve was switched from the sample setting to the leak-check/probe-purge setting, and a post-test leak check was made. The procedures for the post-test leak check of each sampling train were the same as for the pretest leak check except that the vacuum was set at a value greater than that observed during the sample run. At the completion of all post-test leak checks, the flow rates of the test gases at the dilution system were remeasured to confirm steady-state conditions. All data were recorded on appropriate data sheets.

The sorbent traps were disconnected from the sampling train, and the caps were replaced. The ND traps were replaced in their glass culture tubes with Teflon-lined caps. The outside of each ST trap and ND culture tube was marked with the direction of flow during sampling and labeled with the unique sample identification number. The sorbent traps were returned to a metal can containing charcoal, which was sealed, labeled, and stored in a cooler containing ice until the traps were transported to the laboratory at the end of each test day. When the samples arrived at the laboratory, they were logged in as part of the chain of custody procedure, and the metal cans were placed in a refrigerator until samples were ready for analysis. A copy of the log-in sheet was given to the analyst.

No other sampling train components were recovered between dry gas test runs during a given week. At the end of a week's tests, the sampling train glassware and all connecting lines and fittings between the four-way valve and the exit of the secondary condensate flasks were returned to the laboratory for cleaning.

3.2.3 Wet Test Gas System

Variations to the preceding descriptions of equipment and procedures were made to permit the conducting of test runs with moisture added to the dry test gas (wet runs) and ruggedness tests. Half of the ruggedness test samples were also wet runs. Only two of the quad sampling trains were used at a time for conducting wet runs (W1 through W8) and ruggedness tests (R1 through R8). In each run, both trains were either ND or ST types.

Equipment for Wet Runs--

The addition of moisture to the dry test gas did not affect operation of the dry test gas generation system because the moisture was added to the dry test gas between the point where the sample gas was pulled out of the manifold and where it entered the probe liner. Figure 3-8 is a schematic of the moisture generation system used in Runs W1 through W8, the last group of wet runs conducted. For the wet ruggedness tests conducted previously (Runs R3, R4, RR4, R7, and R8), several different variations of this system were used until the final system, as shown, was developed. The changes were made until reproducible moisture contents were obtained.

The other difference in equipment between the wet runs and the dry runs was the heating of sample lines after the heated portion of the probe sheath, the four-way train valves, and the short Teflon connector between the four-way valve and first condenser. Flexible rubber heat tapes were used as the heat source. Slight but insignificant variations occurred between the exact heating of these components. Generally, heat was applied to prevent visible condensation prior to the first condenser.

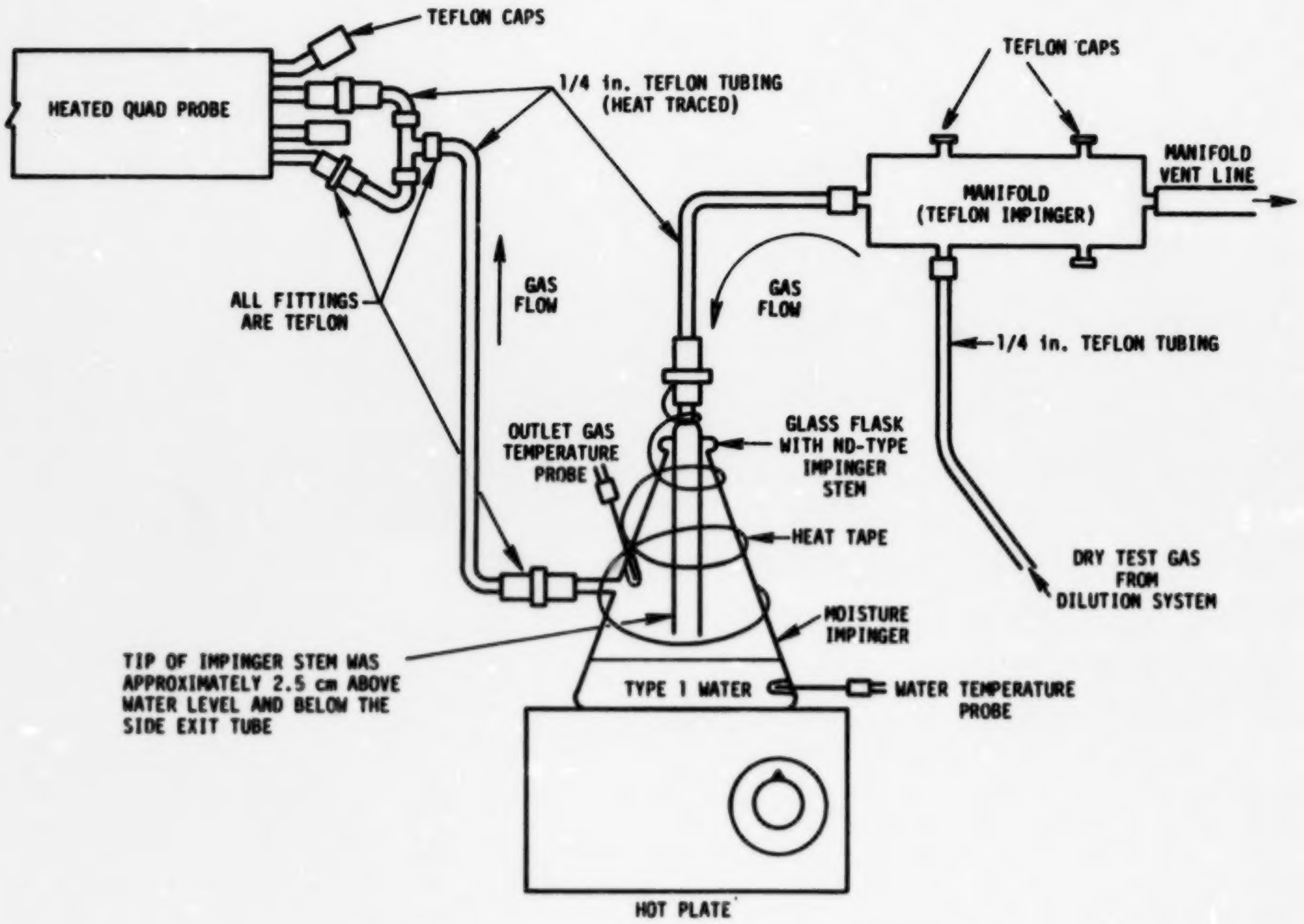

TEFLON CAPS
HEATED QUAD PROBE
1/4 in. TEFLON TUBING (HEAT TRACED)
TEFLON CAPS
MANIFOLD (TEFLON IMPINGER)
MANIFOLD VENT LINE
ALL FITTINGS ARE TEFLON
GAS FLOW
GAS FLOW
1/4 in. TEFLON TUBING
OUTLET GAS TEMPERATURE PROBE
GLASS FLASK WITH ND-TYPE IMPINGER STEM
HEAT TAPE
DRY TEST GAS FROM DILUTION SYSTEM
MOISTURE IMPINGER
TIP OF IMPINGER STEM WAS APPROXIMATELY 2.5 cm ABOVE WATER LEVEL AND BELOW THE SIDE EXIT TUBE
TYPE 1 WATER
WATER TEMPERATURE PROBE
HOT PLATE

Figure 3-8. Moisture generation system.

Procedures for Wet Runs--

Initially, a measured amount (approximately 75 ml) of freshly boiled Type 1 H_2O was added to the moisture impinger, and the equipment was set up as shown in the Figure 3-8. The manifold was purged with dry test gas, and the flow rate of the manifold vent line was measured with a bubble meter. The water flask temperature was set at approximately 75°C, connecting lines were heated to approximately 120°C, and the probe purge was initiated. The manifold vent line flow rate was remeasured. For determination of the dry portion of moisture-laden gas purged through the probes, the difference in manifold vent flow rates when purging and not purging the probes was multiplied times the duration of the probe purge. These data were used later in calculations of moisture content. After the probe purge, the runs were conducted as usual.

At the completion of the post-test leak check for the wet runs, the sampling train and moisture system were disassembled and recovered. For the moisture impinger, the first step in the recovery procedure consisted of determining the final volume (weight) of water remaining by either weighing the impinger on a Mettler balance and subtracting the impinger's tare weight, or by pouring the contents of impinger into a graduated cylinder and measuring the final volume. The difference in volume (weight) of water in the moisture impinger (approximately 20 ml) was combined with sample volumes and purge gas volumes to determine the moisture content of the gas stream sampled. An aliquot of the water remaining in the moisture impinger was placed in a small vial so that the water level was higher than the brim. A Teflon-lined cap was placed on the vial in such a manner that no air bubbles were present within the vial. The vial was then sealed, labeled with the run number, and placed in a cooler of ice until its transfer to the laboratory with the other samples.

The sampling trains were recovered by first removing the sorbent traps as usual. Any water in the sorbent traps was kept inside the traps. The Teflon tubing connection and first condenser coil were disconnected from the four-way valve. The primary condensate collection flask was connected to the bottom of the condenser. The same batch of Type 1 boiled water used in the moisture impinger was used to rinse the Teflon connector and coil into the flask. The volume of rinse water was estimated so that the amount of condensate collected in the flask during a sample run and the rinse volume combined were enough to fill two small glass vials. These vials were filled and stored according to the same procedures followed for the moisture impinger samples. Any excess was discarded.

The total amount of condensate in a sampling train was estimated but not measured because of the small volume and because some of the moisture was retained by the Tenax in the first trap. No moisture was evident in the sampling train component downstream of the primary condensate flask.

The water impinger samples were retained for possible analysis to assess any loss of target compounds in the moisture generation system that would result in a low bias in calculated recoveries. The sampling train condensate samples were kept for possible analysis to determine the amount of any target compounds being retained by the water instead of the Tenax. (Results of selected sample analyses are presented in Appendix D.)

The moisture content of the test gas sampled by each of the paired sampling trains in a given run was estimated in the following manner. First, it was assumed that the gases sampled by each train in a pair had equal moisture contents (percent by volume). This should be a valid assumption because the sampling rates of each train were approximately the same, and the test gas was not split between the two trains until after the moisture had been added to the gas. Second, it was assumed that the average moisture contents of the test gas during the probe purge and sample run were approximately equal. The total amount of water added to the test gas, determined by pre- and post-test measurements of water in the moisture impinger, was then converted to equivalent gas volume. The total amount of dry gas passing through the moisture impinger was the sum of the purge gas volume and the sample volume of both trains. Moisture content of the test gas was calculated by dividing the gas volume of water added by the sum of the dry gas passed through the system and the gas volume of water added.

3.2.4 Blank Samples

During the test series, several different types of blank samples were obtained. Each test week, three pairs of sorbent traps (one Tenax and one Tenax/charcoal trap per pair) were collected and designated as field, trip, and laboratory blanks. The type of sorbent trap used to collect these blanks (ST or ND) was alternated during each week of testing, and at the end of the test series, a set of sampling system blanks and a leak-checked blank were collected.

All of the blank samples were stored at ice temperature in metal cans containing charcoal, in the same manner as samples. (Results of the field, trip, and laboratory blanks are presented in Section 4, and the sampling system blank results are presented in Appendix D.)

Field Blanks--

A pair of sorbent traps was set up in the quad VOST in the same manner as a normal sample. After the VOST was assembled, the traps were removed and replaced in the normal manner. The field blank was returned to appropriate storage and analyzed as a sample. Thus, the field blank received the same potential exposure to contamination from ambient air as the samples.

Trip Blanks--

This pair of traps was not opened at the sampling site, but was left in the metal cans with other sorbent traps while the samples were being collected. Trip blanks were stored and analyzed in a similar manner as samples. Thus, the trip blanks should have been less susceptible to contamination than the field blanks.

Laboratory Blanks--

One pair of sorbent traps was stored in a metal can containing charcoal and refrigerated until analysis was performed with the samples; however, the traps were never removed from the laboratory. Therefore, the laboratory blanks were subject to the least possible contamination or degradation.

Sampling System--

Two pairs each of ST and ND traps were set up in the quad VOST according to normal procedures for samples. The dilution system was set up to use only the ultra-pure air cylinder; i.e., no target compounds were added. The manifold and probes were purged in the usual manner, and a 20-liter sample of air was collected by each train. The sampling system's blank sorbent traps were handled and analyzed in the same manner as the samples were.

Leak-Check System--

A pair of ND traps was set up in the quad VOST in the normal manner except that several fittings were purposely not tightened fully so that the pretest leak check would not be acceptable. Several leak checks were conducted until all fittings were tightened and an acceptable leak check was obtained. The traps were then removed, stored along with other samples, and finally analyzed as a sample.

3.3 SORBENT TRAP PREPARATION, CONDITIONING, AND PRETEST BLANK CHECKING

This subsection describes the preparation of the reagent and materials, the assembly and conditioning of the sorbent traps, and pretest blank-checking of conditioned traps, including the results of the blank checks. Because various combinations of trap-conditioning measures were tried over the course of the laboratory study, recommendations regarding the procedures are also presented at the end of this subsection.

In some cases, the protocol was unclear as to the specific procedures, or it offered alternative procedures that could be selected. The procedures actually used were based on previous experience, on how frequently they were employed by other VOST users (if any), or on EPA's recommendations. In any case, the exact handling of each trap during preparation and conditioning was documented in a log. For example, the VOST protocol specified that ST type traps be thermally conditioned for 8 hours, but it did not indicate (as had previous protocols) whether a single 8-hour treatment or multiple shorter treatments should be used. Because a single treatment was the most straightforward method, this method was used, at least initially.

Assembly of sorbent traps; storage of sorbent, glassware, and assembled traps; and conditioning of sorbent traps took place in a room designated as the VOST preparation room, where no organic solvents were handled or stored.

3.3.1 Reagent and Materials Preparation

Tenax 35/60 Mesh (2,6-Diphenylene Oxide Polymer)--

A single lot of Tenax was used throughout the laboratory study. Raw Tenax as received from the supplier was Soxhlet-extracted for 24 hours with methanol, partially dried under an infrared lamp to avoid sudden, violent boiling of methanol, and then placed in a vacuum oven at 50°C to complete the drying.

One 15-g bottle of the raw Tenax (as received from the supplier) was supplied to each of two independent laboratories for assessment of general Tenax quality. Each laboratory processed the Tenax differently, following its own procedures, and analyzed at least six traps. Both laboratories reported that the Tenax was of typical quality. One laboratory indicated that the benzene content was approximately 20 ng per trap, whereas the other one reported approximately 2 or less ng per similar size trap.

Charcoal--

A single lot of Calgon-Type GW20X50, petroleum-based charcoal was used throughout the study. New charcoal was extracted and dried in the manner just described for Tenax.

The extraction procedures are not recommended for the charcoal, as better blank values have been obtained with unextracted charcoal. Of course, whether extraction is needed may depend on the particular batch of charcoal being used.

O-Rings--

The Viton O-rings used for ST traps were cleaned ultrasonically in a hot, nonionic detergent (Alcojet) solution, rinsed with water, and baked in a vaccum oven at 200°C.

Glassware and Teflon Parts--

All glass parts and Teflon fittings were cleaned with a nonionic detergent, rinsed with water, and then oven-dried at 110°C.

Metal Parts--

C-clips, screens, and ND trap end plugs were cleaned ultrasonically in a nonionic detergent solution; rinsed with water; and heated in a muffle furnace at 400°C.

Glass Wool--

Pyrex wool filtering fiber was Soxhlet-extracted for 16 hours with pentane, partially dried under an infrared lamp, and then placed in a vacuum oven at 100°C to complete the drying.

A preliminary check of the first batch of pentane-extracted glass wool indicated the presence of residual pentane; therefore, the first batch of wool was reextracted and dried as previously described except that the solvent was methanol. Subsequent batches of glass wool were extracted only with methanol.

Additional details of reagent and materials preparation is described in Appendix B.

3.3.2 Assembly and Conditioning of VOST Sorbent Traps

Assembly--

All assembly and packing of sorbent traps was done in a reverse-flow ventilation hood with a charcoal filter on the air intake. The assembly hood was located in the VOST preparation room. Nylon gloves were worn during the assembly steps to avoid contamination with skin oils.

Loading of sorbents into the glass traps was accomplished with a modified rifle-shell loader. The apparatus was calibrated at three different settings to deliver either 1.6 grams of Tenax, 1.0 gram of Tenax, or 1.0 gram of charcoal. Tenax traps were loaded with 1.6 grams of Tenax, and Tenax/charcoal traps were loaded with 1.0 gram of each sorbent. A small section of Teflon tubing was used to transfer the sorbent from the loader into the ND sorbent traps. No tubing was needed for the ST traps, which had larger openings.

For the ST traps, sorbent beds were held in place by stainless steel screens and zinc-coated steel C-clips; for the ND traps, they were held in place by glass wool plugs inserted with the aid of a GC column packing tool. The sorbent beds in the Tenax/charcoal tubes were separated from each other in the same way. Packed sorbent traps were stored in clean glass-culture tubes with Teflon-lined screw caps to prevent contamination between preparation steps. A small plug of clean glass wool was placed in the bottom of the culture tube to cushion the sorbent trap. At this stage of assembly the ST trap consisted of the inner glass tube packed with sorbent. The ST inner trap was not assembled into the protective outer glass trap with O-rings to form the complete ST trap until after the inner traps were thermally conditioned. All of the packed sorbent traps (inside culture tubes) were kept in sealed glass aquariums containing activated charcoal between preparation steps.

All sorbent traps were labeled with a numeric code by etching the glass to facilitate documentation of the exact handling of each trap during preparation and conditioning. After each trap was packed, the trap packer recorded the trap and culture tube numbers, reagent batch numbers, and storage location in the log book.

Conditioning Procedures--

Sorbent traps were conditioned by purging with approximately 30 ml/min of nitrogen at elevated temperatures. Different conditioning procedures were used for the ST and ND traps. All conditioning batch data were recorded in log books to document the treatment of each trap. Several combinations of conditioning times and temperatures were tried over the course of the laboratory study in efforts to obtain lower and more consistent blank values.

The ST inner traps were conditioned in a Nutech 14-chamber multiple desorber at 250°C. At the end of a conditioning period the hot traps were removed from the desorber and replaced in the culture tubes to cool. The sorbent traps were then fully assembled by placing two of the smaller O-rings on the inner trap, pushing it into the protective outer glass trap, and capping both ends. Nylon gloves were worn during this assembly step to avoid contamination with skin oil. For some conditioning batches, the fully assembled ST traps received additional thermal conditioning (up to 15 at a time) on an E-manifold at 150°C to remove any contamination during trap assembly.

Initially, the ST traps were conditioned for a single 8-hour period in the multiple desorber followed by a single 2-hour period on the manifold. Subsequently, other combinations of treatment intervals were tried; these consisted of a single 8-hour period in the multipler desorber followed by multiple heating periods on the manifold, four 2-hour periods in the multiple desorber followed by a single interval on the manifold, multiple intervals on both the desorber and manifold, single intervals in the desorber for 16 and 24 hours (no manifold conditioning), and multiple extended intervals in the desorber (no manifold conditioning). For multiple heating intervals, the trap was allowed to cool to room temperature between periods. An evaluation of the pretest blank-check results (presented later) indicated that no particular combination was clearly superior to any other; however, conditioning on the manifold did not seem to be necessary.

All conditioning of the ND traps was performed on an E-manifold holding up to 15 traps per batch at a temperature of 190°C. All Tenax/charcoal traps conditioned on the manifold (either ND or ST) were positioned so that the purge gas entered the charcoal end first.

The initial conditioning of ND traps consisted of a single heating period of approximately 16 hours. Other combinations tried during the laboratory validation included multiple 16-hour heating intervals, a 16-hour period followed by one or more 2-hour heating periods, a 24-hour period followed by one or more 2-hour periods, and a single conditioning period of approximately 28 hours. One pair of traps was even conditioned for a single 60-hour period. For any multiple heating intervals the traps were cooled to room temperature between periods. Based on an evaluation of pretest blank data, a single conditioning period of 28 hours or more is recommended. A summary of pretest blank check data for all traps actually used as samples is presented in the following subsection on pretest blank checking.

All ND and ST traps were stored for at least 24 hours between conditioning and blank-checking. The leak-checking step specified in the protocol was performed during the blank-checking process rather than during the conditioning steps.

More detail on the conditioning apparatus and procedures is included in Appendix B.

3.3.3 Pretest Blank-Checking

Two general blank-checking procedures are included in the VOST protocol. The procedure that is generally more applicable to the ST configuration was not used because it was not quantitative. This procedure involves monitoring the effluent from a heated ST trap by GC/FID until the concentration is less than the approximate detection limit. For the ST traps, the advantage of using the effluent monitoring method is that any trap contamination picked up during final trap assembly (which is not necessary for ND traps) can be desorbed and will not be included in the final blank value. The procedure more applicable to the ND traps consists of cryogenically trapping organic compounds in the effluent from a heated trap and quantitating the amount of organics by GC/FID. The cryogenic approach was adapted for use with both trap types during the laboratory study to ensure comparable results. Equitable application of the cryogenic blank-check method for ST traps required the addition of the extra manifold conditioning step initially, to remove any contamination picked up during assembly.

One pair of ND and ST traps from each week's conditioning batches were blank-checked on the GC/MS analytical system instead of the GC/FID system as a quality assurance check. The ND traps blank-checked by GC/MS were included with the other traps that were blank-checked by GC/FID and stored until ready for use. Because the ST type traps had to be disassembled for blank checking by GC/MS, these traps were returned to the preparation and conditioning area for reassembly and use at a later date.

Discussion--

Blank results were determined for three specific compounds by comparison with calibration standards: benzene, toluene, and tetrachloroethylene.

Because benzene and toluene are generally considered to be inherent contaminants in Tenax, blank levels of these two materials were used to determine the general cleanliness of the traps. Tetrachloroethylene was selected because it was a designated target compound, was a frequent contaminant in the ambient laboratory air, and had a reasonable response on the GC/FID. Although bromofluorobenzene was specified in the protocol, it was not used because it did not benefit this particular project. At the beginning of the laboratory study, all six target compounds were evaluated during the blank checks; however, vinyl chloride, trichlorofluoromethane, chloroform, and carbon tetrachloride were soon eliminated from the GC/FID blank check criteria because their response or chromatographic separation was inadequate. In any case, these compounds were not expected to be present in any of the blanks.

The protocol specified a desorption temperature of 190°C, and initial checks were made at that temperature; however, the ST traps were found to have higher degrees of overall contamination than the ND traps. Several blank runs were made on a set of ST glass traps and O-rings without any sorbent to determine whether this difference was due to the Viton O-rings. These tests confirmed that the O-rings were contributing to the ST blank results, especially those for toluene. The effect of temperature on O-ring contamination was investigated by replumbing the blank-check system so that the effluent from the desorbed traps was routed directly to the GC column. A distinct improvement in GC/FID output was noted as the desorption temperature was decreased from 190° to 150°C, but not at lower temperatures. Thus, for minimization of the contribution of the Viton O-rings, the blank-check desorption temperature was set at 150°C. A pair of ST traps was blank-checked in the normal manner at 150°C and again at 190°C. Because the repeat blank check at 190°C came out completely clean except for the same initial peak as in a system blank, it was determined that 150°C yielded representative results. A calibration recovery check at 150°C was made by comparing the response of an on-column standard injection and that of a standard loaded onto a Tenax trap. Recovery percentages were 130 percent for benzene and 93 percent for tetrachloroethylene (toluene was not run on-column).

System blanks (desorption and analysis cycles without any VOST traps) were run periodically during the study. Chromatograms from the system blanks showed a relatively clean system with a small peak eluting immediately at the start of a run. No contaminants were present in the system blanks that would interfere with the actual blank checks.

Static gas bottle standards (instead of methanolic ones) were used to calibrate the GC/FID system to avoid large methanol peaks on the chromatograms.

The GC/FID blank-check system yielded excellent responses to benzene and toluene. The protocol criteria limit for benzene was less than 2 ng per pair of sorbent traps. This level was easily measurable at an average strip chart peak height response of approximately 10 mm. The response to toluene was similar, but a little lower. The response to tetrachloroethylene, however, was such that 2 ng of this compound typically would yield a peak height of less than 2 mm (calculated based on the response of the 79-ng standard). This response level made it difficult to determine the presence of tetrachloroethylene with any certainty.

The total amount of chromatographable compounds in each blank check was not determined in this laboratory study. If the protocol blank-check criteria limit of less than 10 ng of chromatographable compounds (quantitated as benzene) were followed strictly, many of the traps would not have been usable.

It should be emphasized that none of the other peaks [save those for benzene and tetrachloroethylene (perc)] interfered with the laboratory validation. The blank-check acceptance criterion used throughout the study was less than 5 ng each of benzene and perc per trap pair. At times this criterion was not met, and the best-available traps were used. The decision to use or reject traps in these instances was based on the relative amounts found on the blank and the amount to be sampled. For example, a blank of 30 ng benzene would represent only 3 percent of the total amount sampled during a test at 15 ppb, but it would be roughly equal to the amount sampled during a test at 0.5 ppb.

Table 3-2 summarizes the pretest blank-check data on each trap pair used as a sample or blank, except for those used in the blank evaluation. Tubes containing used Tenax have an "R" in the tube identification number. Virtually all of the blank checks conducted by GC/MS that are included in the table show higher levels of benzene than the GC/FID blank checks. This effect may be related to zero offset in the the GC/MS calibration curve for benzene. The nominal calibration points for the high-level benzene curve were approximately 250, 1000, and 2500 ng; therefore, a small shift in the curve could have significantly affected the low-level portion of the curve.

The blank-check chromatograms were generally characterized by several large peaks that eluted within the first two minutes of the run. These compounds would have masked any vinyl chloride that might have been present, but otherwise did not interfere with the interpretation of blank results. Most of the time this group of peaks could not be quantified because they were off-scale. Two other peaks eluted between these early peaks and benzene. Their frequency and magnitude of appearance were highly variable, and they

TABLE 3-2. SUMMARY OF PRETEST BLANK CHECK VALUES FOR TRAPS USED IN THE PRECISION AND ACCURACY OR RUGGEDNESS TESTS

Run No.	Paired tube Nos.		Blank values, ng per pair			Blank check method
			Benzene	Tetrachloroethylene	Toluene	
Q1	ND-T-147	ND-TC-128	1.2	1.5	0.2	FID
Q1	ND-T-113	ND-TC-43	2.0	a	a	FID
Q1	ST-T-47	ST-TC-45	4.1	3.2	1.6	FID
Q1	ST-T-61	ST-TC-40	3.0	3.2	1.6	FID
Q2	ND-T-11	ND-TC-48	56.8	0.2	b	MS
Q2	ND-T-149	ND-TC-20	1.6	a	a	FID
Q2	ST-T-110	ST-TC-70	<2[c]	b	b	FID
Q2	ST-T-30	ST-TC-142	1.2	3.1	0.2	FID
Q3	ND-T-126	ND-TC-76	4.8	1.6	0.5	FID
Q3	ND-T-47	ND-TC-110				
	(47/50)[d]		25.9	a	b	MS
	(55/110)[d]		2.7	b	b	FID
Q3	ST-T-111	ST-TC-43	<2[c]	b	b	FID
Q3	ST-T-168	ST-TC-135	2.9	12.6	1.6	FID
Q4	ND-T-2	ND-TC-82	29.5	21.6	b	MS
Q4	ND-T-119	ND-TC-50				
	(119/118)[d]		23.9	a	b	MS
	(47/50)[d]		25.9	a	b	MS
Q4	ST-T-4	ST-TC-21	<20[c]	b	b	FID
Q4	ST-T-29	ST-TC-167	<2[c]	b	b	FID
Q5	ND-T-35	ND-TC-28	4.2	8.8	3.6	FID
Q5	ND-T-63	ND-TC-94	4.6	1.3	4.2	FID
Q5	ST-83	ST-TC-88	2.1	4.9	3.3	FID
Q5	ST-22	ST-TC-16	3.5	3.1	2.8	FID
Field blank	ND-T-134	ND-TC-22				
	(134/118)[d]		<2	b	b	FID
	(119/22)[d]		<1	b	b	FID
Field blank	ST-T-75	ST-TC-136	2.7	b	b	FID
Trip blank	ND-T-40	ND-TC-51	20.7	1.3	b	MS
Q6	ND-T-135	ND-TC-109	0.4	4	0.8	FID
Q6	ND-T-8	ND-TC-24	2.4	a	2.1	FID
Q6	ST-109	ST-TC-1	1.9	11.5	8.7	FID
Q6	ST-33	ST-TC-139	2.3	8	7	FID
Q7	ND-T-62	ND-TC-107	0.6	a	2.1	FID
Q7	ND-T-44	ND-TC-34	0.4	a	2.1	FID
Q7	ST-48	ST-TC-118	2.3	10.3	5.7	FID
Q7	ST-20	ST-TC-54	0.8	5.7	7.6	FID
Q8	ND-T-16	ND-TC-79	0.4	6.0	2.0	FID
Q8	ND-T-67	ND-TC-120	0.5	2.3	2.7	FID
Q8	ST-38	ST-TC-60	1.2	9.6	16	FID
Q8	ST-137	ST-TC-82	1.2	5.8	8.5	FID
Field blank	ST-123	ST-TC-101	0.4	5.8	16.8	FID
Field blank	ND-T-102	ND-TC-88	0.3	5.7	2.1	FID
Trip blank	ST-67	ST-TC-148	2.8	5.8	8.2	FID
W1	ND-T-113	ND-TC-170	1.0	a	2.9	FID
W1	ND-T-89	ND-TC-71	0.5	1.8	1.4	FID
W2	ST-106	ST-TC-116	a	1.8	1.3	FID
W2	ST-102	ST-TC-154	0.6	9.4	7.4	FID
W3	ST-146	ST-TC-44	1.1	12.1	4.9	FID
W3	ST-9	ST-TC-24	1.0	12.7	7.5	FID
W4	ND-T-70	ND-TC-154	0.5	3.5	3.3	FID
W4	ND-T-64	ND-TC-163	0.5	12.7	1.0	FID
Trip blank	ND-T-6	ND-TC-172	0.5	7.0	2.4	FID
Field blank	ST-105	ST-TC-136	0.4	3.4	3.9	FID

(continued)

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TABLE 3-2 (continued)

Run No.	Paired tube Nos.		Blank values, ng per pair			Blank check method
			Benzene	Tetrachloro-ethylene	Toluene	
W5	ND-T-36	ND-TC-155	0	6.3	1.1	FID
W5	ND-T-60	ND-TC-118	1.4	12.7	1.4	FID
W6	ST-14	ST-TC-53	1.2	1.6	2.7	FID
W6	ST-130	ST-TC-56	2.7	3.2	a	FID
W7	ST-31	ST-TC-98	a	a	a	FID
W7	ST-172	ST-TC-94	a	1.6	2.0	FID
W8	ND-T-179	ND-TC-193	a	12.8	0.6	FID
W8	ND-T-149	ND-TC-20	1.4	15.9	2.1	FID
Lab blank	ST-12	ST-TC-152	a	1.9	6.1	FID
Lab blank	ND-T-186	ND-TC-194	0.6	24	1.1	FID
Field blank	ST-201	ST-TC-75	0.5	3.2	6.5	FID
Field blank	ND-T-151	ND-TC-161	0.2	3.2	0.3	FID
Trip blank	ND-T-190	ND-TC-129	a	a	2.0	FID
Lab blank	ND-T-183	ND-TC-160	1.8	9.8	1.1	FID
R1	ND-T-95	ND-TC-111	0.7	2.3	0.4	FID
R1	ND-T-57	ND-TC-129	0.9	a	0.6	FID
R2	ST-R111	ST-TC-R40	0.6	a	0.4	FID
R2	ST-R61	ST-TC-R142	0.7	2.0	2.9	FID
R3	ST-159	ST-TC-161	0.9	1.0	1.9	FID
R3	ST-164	ST-TC-176	2.2	3.4	2.5	FID
R4	ND-T-R47	ND-TC-R128	0.5	a	0.2	FID
R4	ND-T-R126	ND-TC-R110	0.4	a	0.2	FID
RR4	ND-T-R57	ND-TC-R50	0.1	1.6	0.2	FID
RR4	ND-T-R33	ND-TC-R85	0.5	0.9	a	FID
Field blank	ND-T-15	ND-TC-84	8.1	0.2	a	MS
Field blank	ST-171	ST-TC-119	4.3	13.3	10.3	FID
Trip blank	ST-202	ST-TC-141	0.5	23	4.7	FID
R5	ST-4	ST-TC-142	1.0	12.1	5.5	FID
R5	ST-R111	ST-TC-R21	1.0	22	15.2	FID
R6	ND-T-31	ND-TC-19	0.4	1.1	0.2	FID
R6	ND-T-10	ND-TC-9	0.7	4.3	0.4	FID
R7	ND-T-23	ND-TC-R76				
	(23/124)[d]		0.4	0.6	0.4	FID
	(R95/R76)[d]		0.2	11.7	1	FID
R7	ND-T-R2	ND-TC-R82	0.4	0.5	0.7	FID
R8	ST-165	ST-TC-64	0.8	a	3.1	FID
R8	ST-125	ST-TC-173	1.5	a	5.7	FID
Trip blank	ND-T-81	ND-TC-69	0.5	5.3	1.1	FID
Field blank	ST-41	ST-TC-163	1.5	4.5	a	FID
Field blank	ND-T-27	ND-TC-124				
	(24/92)[d]		0.5	5.3	0.6	FID
	(124/23)[d]		0.4	0.6	0.5	FID
RLC-Q4[e]	N-DT-187	ND-TC-158	1.4	28.7	0.6	FID
BLKST[f]	ST-149	ST-TC-120	1.0	1.0	1.0	FID
BLKST[f]	ST-126	ST-TC-35	0.8	4.8	5.3	FID
BLKND[f]	ND-T-158	ND-TC-197	0	14.3	1.8	FID
BLKND[f]	ND-T-174	ND-TC-92	9.0	33.3	0	FID

[a] None detected.

[b] Undetermined.

[c] Estimated from calibration data on different day.

[d] Traps were not blank checked as a pair prior to testing. Blank values are shown for the two pairs in which they were blanked.

[e] Pair used to determine effect of repeated leak checks.

[f] Blank train samples.

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represented approximately 20 ng as benzene on the average. Other peaks were attributed to common solvents known to be used in our building; e.g., acetone, methylene chloride, and hexane. Tetrachloroethylene is also used in a blueprint shop located in the building, which probably explains the levels of that compound detected during the blank checks. The presence of these ambient compounds in the blank was highly variable. In any case, only the tetrachloroethylene caused any interference with the test sample results.

3.3.4 Development of Final Conditioning and Handling Procedures

After the laboratory evaluation tests were completed, the charcoal preparation and sorbent trap handling procedures were evaluated in an effort to improve blank values of conditioned sorbent traps and to minimize environmental contamination of the clean traps. Clean traps could become contaminated during handling in a laboratory where an "organic-free area" does not exist and the air contains commonly used laboratory solvents or during field tests at a plant site. The problem of highly contaminated field blanks is not uncommon with the VOST.

The new procedures include a preheating step for the charcoal sorbent in place of methanol-extraction, and purging the trap storage containers. Results of the comparison between charcoal extracted with methanol and unextracted charcoal are described in Appendix B.

The effectiveness of the new preparation and handling procedures is illustrated by comparing blank-check chromatograms (Figures 3-9 and 3-10). Figure 3-9 is a blank check of an ND trap pair conditioned for a 28-hour period at 190°C according to the old handling procedures, i.e., no purging of the culture tubes, and containing methanol-extracted charcoal. The peak for hexane, a common laboratory solvent, was the only peak that could be identified represented approximately 20 ng as benzene on the average. Other peaks were attributed to common solvents known to be used in our building; e.g., acetone, methylene chloride, and hexane. Tetrachloroethylene is also used in a blueprint shop located in the building, which probably explains the levels of that compound detected during the blank checks. The presence of these ambient compounds in the blank was highly variable. In any case, only the tetrachloroethylene caused any interference with the test sample results.

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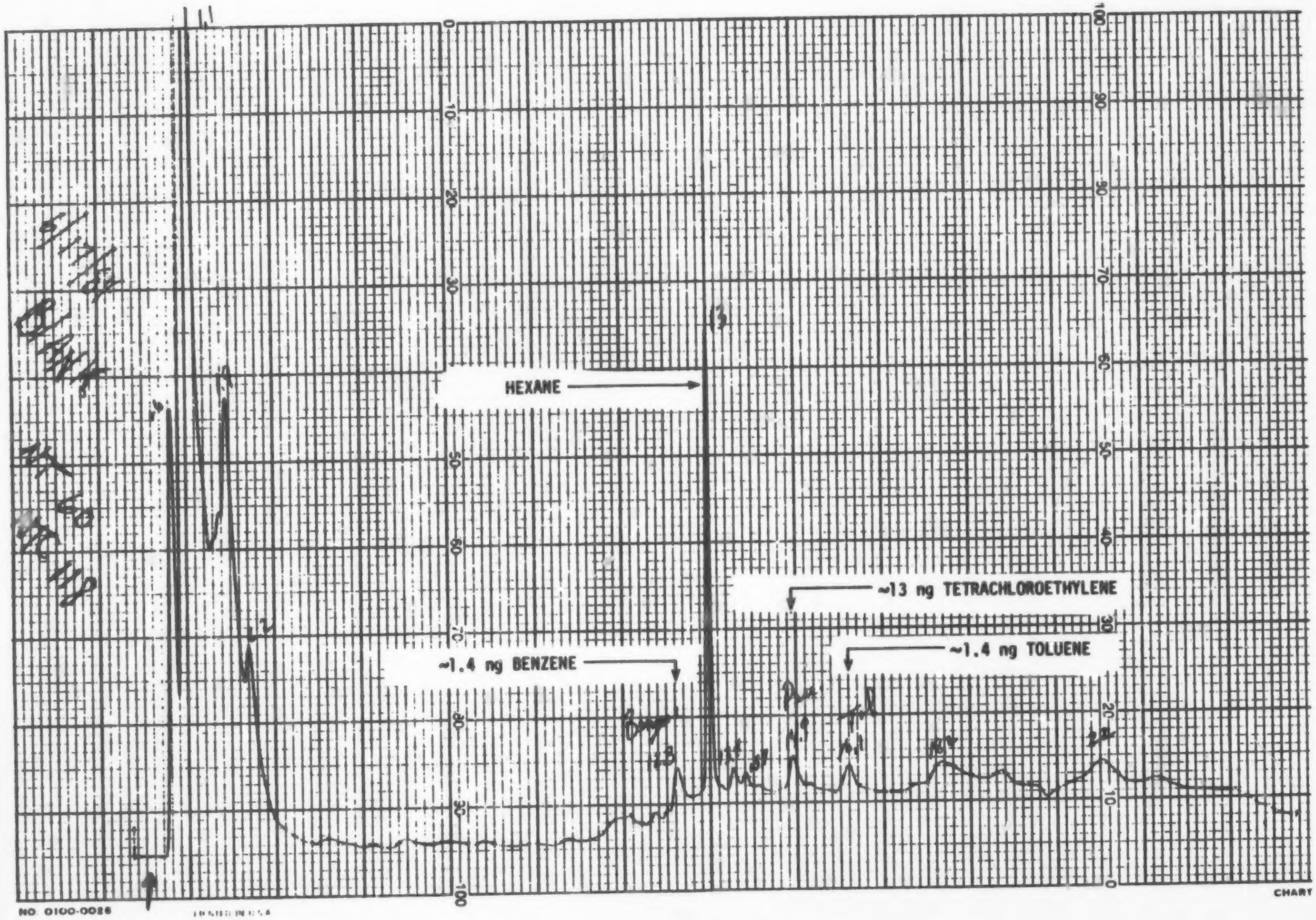

Figure 3-9. ·Blank-check chromatogram of ND trap pair (T60 and TC118) on 6/17/84 using old procedures.

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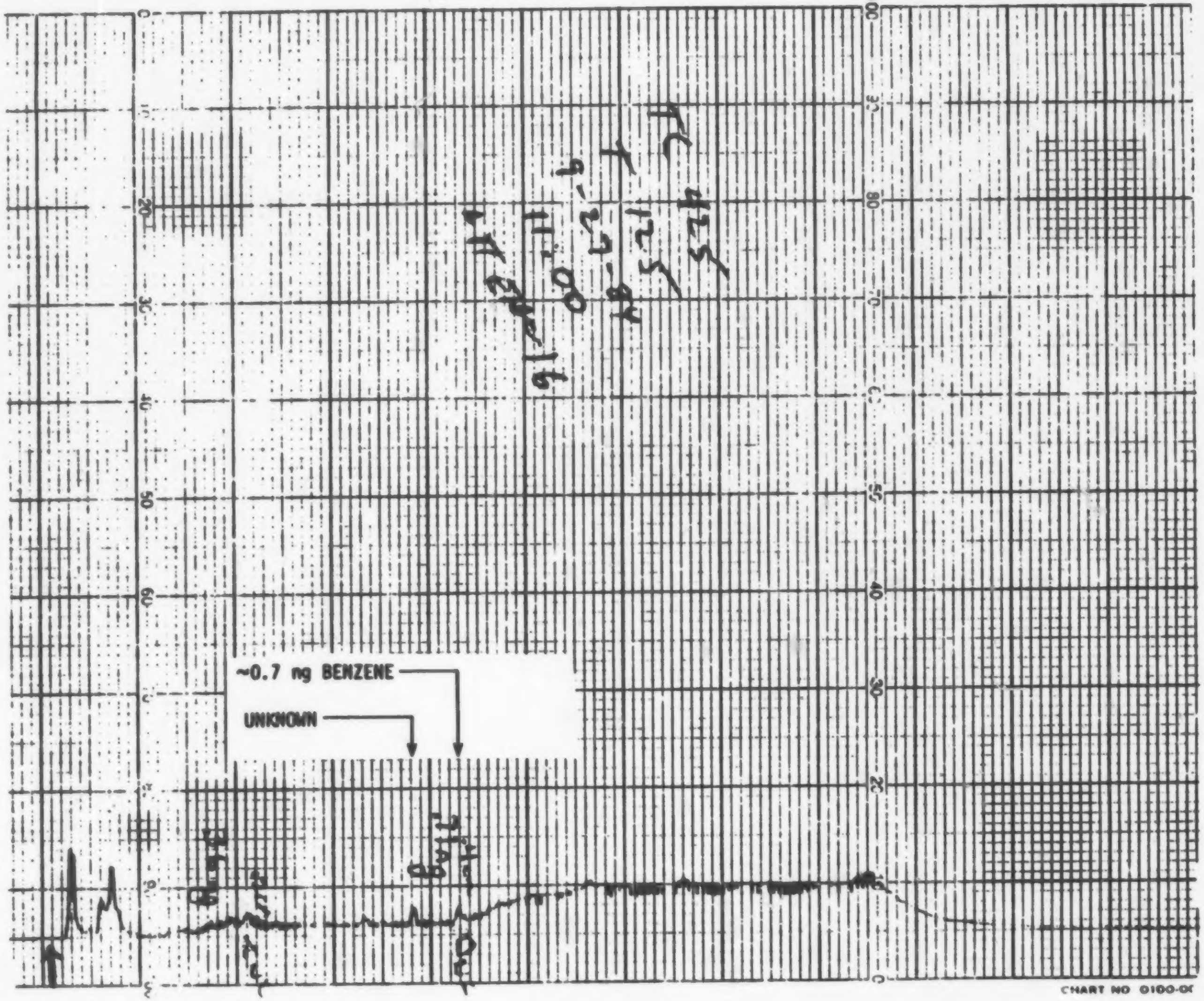

Figure 3-10. · Blank-check chromatogram of a pair of ND traps prepared by use of new procedures.

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other than those for the three calibration standard components. The large, multicomponent peak eluting early in the chromatogram has been attributed to the charcoal. The chromatogram shown in Figure 3-10 represents a blank check of an ND trap pair conditioned in a similar manner, but by use of the new handling procedures, and containing unextracted charcoal. Although different GC columns were used in the two blank checks, and the retention times cannot be compared, the magnitude of the peaks in both chromatograms can be compared on a roughly equal basis. This comparison clearly indicates that the new method blank-check values are significantly better.

The purging of trap storage containers may prove to be beneficial in the reduction of field blanks if the containers also are purged in the field. This will be determined during the field test phase.

3.4 ANALYTICAL PROCEDURES

Analytical procedures in the protocol are generally those described in Method 624 plus additional steps for desorption of Tenax and Tenax/charcoal sorbent traps. Figure 3-11 is a schematic diagram of the analytical system. Each sample sorbent trap (either Tenax or Tenax/charcoal) was spiked with an internal standard using a flash vaporization device and thermally desorbed for 10 minutes at 180°C with organic-free helium gas. The gas, which had a flow rate of 40 ml/min was bubbled through 5 ml of organic-free water and trapped on an analytical sorbent trap. After the 10-minute desorption period, the analytical sorbent trap was rapidly heated to 180°C with the carrier gas flow reversed so that the effluent flow from the analytical trap was directed into the GC/MS. The volatile organics were separated by temperature-programmed gas chromatography and detected by low-resolution mass spectrometry. The mass of each target compound was calculated by the internal standard technique.

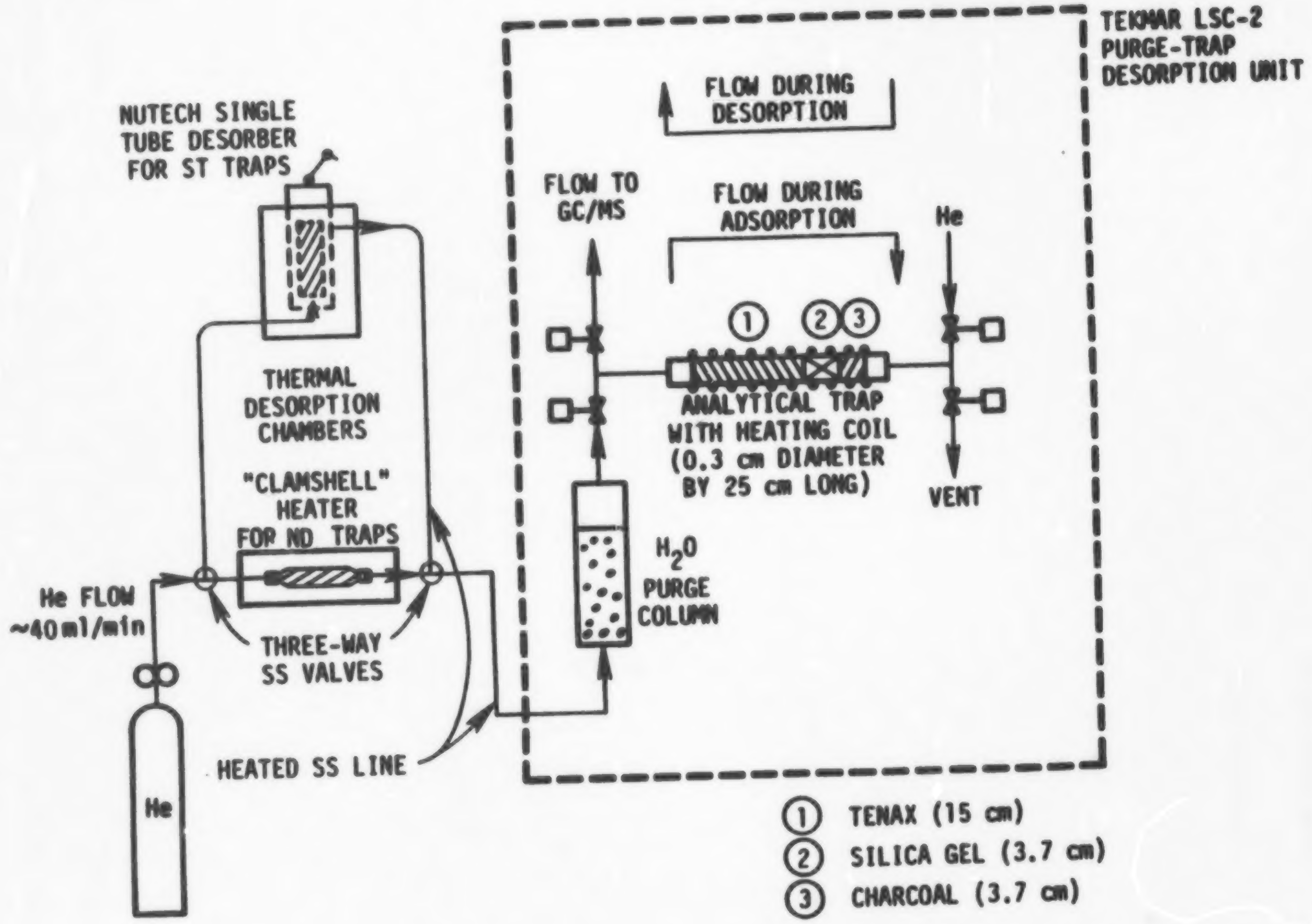
NUTECH SINGLE TUBE DESORBER FOR ST TRAPS
THERMAL DESORPTION CHAMBERS
"CLAMSHELL" HEATER FOR ND TRAPS
He FLOW ~40 ml/min
THREE-WAY SS VALVES
HEATED SS LINE
He
TEKMAR LSC-2 PURGE-TRAP DESORPTION UNIT
FLOW DURING DESORPTION
FLOW TO GC/MS
FLOW DURING ADSORPTION
He
① ② ③
ANALYTICAL TRAP WITH HEATING COIL (0.3 cm DIAMETER BY 25 cm LONG)
VENT
H_2O PURGE COLUMN
① TENAX (15 cm)
② SILICA GEL (3.7 cm)
③ CHARCOAL (3.7 cm)

Figure 3-11. Schematic of VOST sorbent trap desorption and analysis system.

The GC/MS system used was a Finnigan Model 4023 with quadrupole mass spectrometer. The temperature-programmable gas chromatograph included a septum-plugged tee fitting through which "on-column" injections could be made for recovery and tune checks. The glass column was 1.8 meters long with a 2-mm i.d. and was packed with 1 percent SP-1000 on Carbopak B (60/80 mesh). Operating conditions for suitable chromatography were determined by analysis of preliminary samples. The temperature program was set at 50°C for 2 minutes, ramped at 10° per minute up to 220°C, and held for 1 minute to yield a total run time of 20 minutes. The GC to MS interface was an all-glass jet separator. The mass spectrometer was scanned from 35 to 335 m/e (mass to charge ratio) every 2 seconds. Two electron multiplier voltage settings were used during the laboratory study to modify detector sensitivity so that the range of expected target compound levels would be within the linear working range of the instrument.

The data acquisition and processing system that controlled the mass spectrometer consisted of a Data General Nova 3 computer with a Perkin-Elmer/-Wangco 10-megabyte dual-disk drive that runs Finnigan Incos Software. This system permitted continuous acquisition and storage of all mass spectra obtained during chromatographic analyses. It also permitted the searching of data files for ions of selected masses and the searching of certain scans for comparison to the NBS library of mass spectra for best matches. It also permitted plots and integrations of peak areas of Extracted Ion Current Profiles.

3.4.1 Sample Desorption and Analysis

A sample sorbent trap, either a Tenax or a Tenax/charcoal trap, was loaded with an internal standard, placed in the appropriate thermal desorption oven, and desorbed by heating to 180°C for 10 minutes while purging with helium gas at approximately 40 ml/min. The ND traps were connected to the desorber system lines outside of the oven, with no purge flow. At the beginning of the desorption period, the ND traps were placed into the hot oven and the purge flow was started immediately. The ST traps were placed into the hot Nutech desorber with no purge flow, and then the purge flow was started immediately. The traps were placed in the ovens in such a way that the purge gas passed through the sorbent trap in the direction opposite to that of sample collection (or standard loading); i.e., the inlet during sampling became the outlet during analysis. The desorbed sample components passed into the bottom of the water column, were purged from the water, and were collected on the analytical sorbent trap. After the 10-minute desorption period, the concentrated sample was desorbed from the analytical sorbent trap into the GC/MS system by reversing the direction of helium flow through the analytical trap (approximately 40 ml/min) and rapidly heating the trap to approximately 180°C. While the concentrated sample is being desorbed from the analytical trap into the GC/MS, the sample traps are still in the heated oven with no purge flow. (It is suspected that inherent benzene contamination of the Tenax may be released and not removed during this period. The lack of flow during this period is inherent in the design of the commercially available purge and trap devices used with EPA Method 624.) While the sample stream was being separated into its various components on the GC column, the analytical sorbent trap was undergoing a purged bake-out at approximately 220°C in preparation for the next analysis. The separated sample components passed through a glass jet separator, where the helium was removed from the sample stream. The sample components were ionized and detected by the mass spectrometer.

Quantitation was performed by the internal standard method. The total nanograms per trap of each target compound was determined from a quadratic fit of the respective calibration curve. This procedure is part of the GC/MS software. The data for each sample analysis consisted of a Reconstructed Ion Chromatogram (RIC), the calculated areas of each peak on the RIC, an Extracted Ion Current Profile (EICP) of the primary ion of each target compound and internal standard, a quantitation list containing the principal ion area and total nanograms for each target compound present (based on the presence of the principal ion) and the internal standard, and the mass spectral fragmentation pattern of each target present in the sample. Spectra were also obtained for other selected peaks that appeared in the RIC for possible identification. In addition to sorbent traps, several aqueous condensate samples were also analyzed. Water samples were introduced into the glass purge vessel of the Tekmar purge and trap unit and analyzed in a similar manner in accordance with EPA Method 624. The target compounds in the water samples were quantified by using a response factor based on low-level, single-point calibration.

3.4.2 GC/MS Calibration

Standard Loading--

Because quantitation was based on the internal standard technique, all analyses (calibrations, sample analyses, and blanks) included an internal standard. For analyses of sorbent traps, standards were first loaded onto the traps. For other analyses, the internal standards were injected by syringe into either the water purge vessel or the tee at the head of the GC column, depending on the purpose of the analysis.

Calibration and internal standards were loaded onto the sorbent traps by use of the flash evaporation apparatus (Figure 3-12). The device described

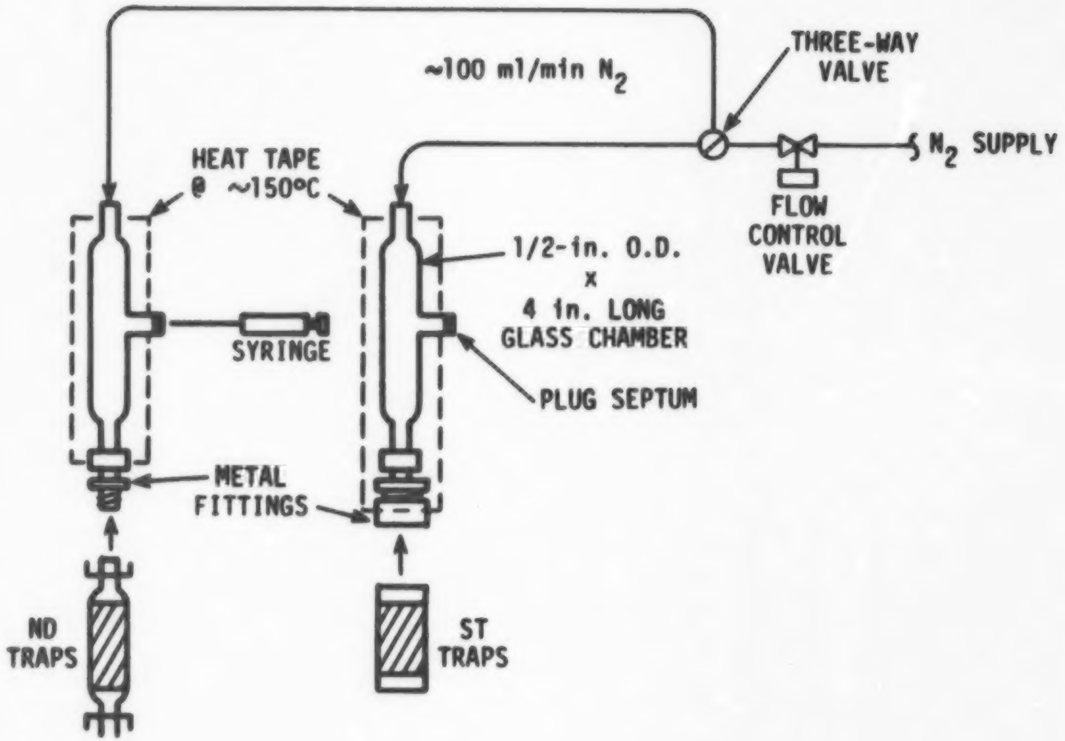
THREE-WAY VALVE
~100 ml/min N2
N2 SUPPLY
FLOW CONTROL VALVE
HEAT TAPE @ ~150°C
1/2-in. O.D. x 4 in. LONG GLASS CHAMBER
SYRINGE
PLUG SEPTUM
METAL FITTINGS
ND TRAPS
ST TRAPS

Figure 3-12. Flash evaporation apparatus for loading standards onto sorbent traps.

in the protocol, an injection port of a GC, was not used because a spare GC was not available and because a GC port is not readily adaptable for loading both ND and ST traps (as required in this study). Carrier flow was set at 100 ml/min so that either chamber volume (approximately 25 ml) was well swept in a 1-minute loading interval. Because the internal standards are loaded onto traps containing samples, the total volume of carrier gas used to load the standard should be minimized to prevent breakthrough of sample components. A total carrier gas volume of 25 ml was specified in the protocol for the GC injection port apparatus; however, a volume of 100 ml was used during the laboratory study to flush the relatively large chamber of the flash evaporation chamber used (approximately 25 ml). Because the 100-ml carrier volume represented only 0.5 percent of a 20-liter sample or 2 percent of a 5-liter sample, the potential loss of sample due to breakthrough during loading of internal standard was minimal.

As specified in the protocol, the "solvent flush" technique was used to load methanolic standards. In addition, the volume of liquid injected should be at least approximatley 30 percent of the syringe capacity to minimize error in liquid volume measurements. Methanolic standards were made up to permit 4-μl volumes of all internal and calibration standards (approximately 40 percent of the syringe capacity).

The protocol did not specify whether the internal standard should be included in the same methanol solution as the mixture of target compounds. In this study (as previously stated) the internal standards were prepared in a separate methanolic solution. Simultaneous injection of both internal standard and target compound calibration standard aliquots was accomplished as follows: about 1 μl of methanol was pulled into a 10-μl syringe for solvent flush, followed by an air space, a 4-μl target compound aliquot, an air space, a 4-μl aliquot of the internal standard, and a final air space. Both standard aliquots were measured by difference in the syringe barrel markings. The entire contents of the syringe were then injected into the flash-evaporation chamber. The methanolic injection was immediately followed by an injection of a gaseous (30.6 ppm in N_2) vinyl chloride standard. The vinyl chloride gas standard aliquots were withdrawn from a dynamic flow of gas from the calibration gas cylinder. A gas-tight syringe was inserted into a tee fitting equipped with a septum plug to withdraw a standard vinyl chloride aliquot (as shown in Figure 3-13). A total of 100 ml of carrier gas was passed through the chamber and trap after the VC injection. Sample traps were loaded in a similar manner except that only the internal standard was loaded.

Calibration Levels--

The protocol states that calibration standards should be prepared so they bracket the working range of the analytical system. However, the linear working range of many GC/MS systems is variable, depending on the preamplifier setting and the electron multiplier voltage. The protocol should be rewritten to indicate that the linear working range of the analytical system should be adjusted to the expected concentrations of target compounds in the samples, and thus, the calibration standards should be prepared to bracket this range. In practice, the desired working range can be determined by analysis of a set of preliminary samples. For the laboratory study the amount of target compounds expected to be in each sample (Tenax and Tenax/-charcoal combined) were known, based on the concentration of the test gas

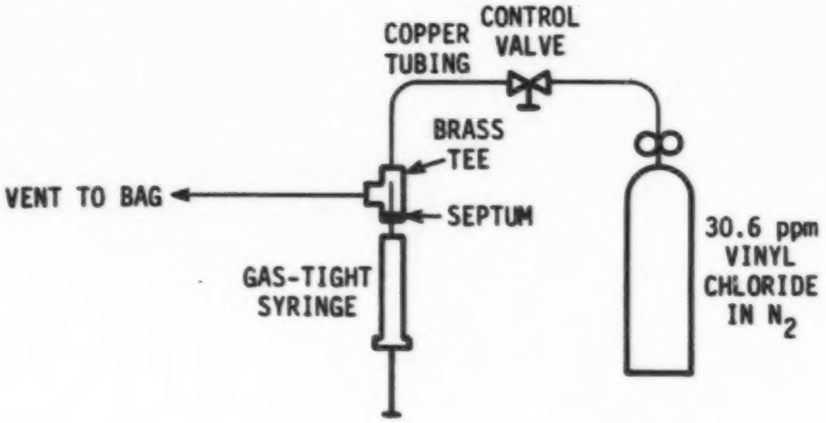
COPPER TUBING
CONTROL VALVE
BRASS TEE
VENT TO BAG
SEPTUM
GAS-TIGHT SYRINGE
30.6 ppm VINYL CHLORIDE IN N_2

Figure 3-13. Aliquoting apparatus for vinyl chloride gas cylinder calibration standard.

(0.5 or 15 ppb) and the sample volume. During a given week of testing, all samples (except blanks) were collected at one nominal test gas concentration. To obtain optimum results, the GC/MS analytical system was calibrated accordingly; one level of calibration standards was used for 15-ppb samples, and a lower level was used for 0.5-ppb samples. For example, the three-point high-range calibration curve was generated by using standards containing nominally 2500, 1200, and 500 (or 250) ng of each target. The low-range curve for 0.5 ppb samples was generated by using nominal standards of 500 (or 250), 100, and 20 ng. Internal standard levels differed for each curve; they were nominally 1000 ng for the high-range curves and 250 ng for the low-range curves. Two different levels of calibration curves were generated because the working range of the instrument could not be extended to be both sensitive at the low end for low-level samples and also linear at the high end for high-level samples. If the instrument was sensitized to detect low levels, the MS tended to become saturated when high-level samples were analyzed.

The ranges of the calibration curves for each target compound could have been made much tighter because the expected amounts in each sample were known; however, doing so would not have been representative of actual unknown sample analysis. Nevertheless, it is important that the instrument calibration range be optimized as much as practically possible to obtain the best results. Obviously, an instrument calibrated between 500 and 2500 ng probably will not analyze a 50-ng sample with the accuracy and reproducibility that could be achieved on an instrument calibrated between 20 and 250 ng.

Types of Calibration Curves--

The protocol requires separate calibrations for Tenax and Tenax/charcoal traps if samples are to be analyzed separately. This proved to be a valid requirement for ST traps, but not for the ND traps. If a given amount of compound was loaded onto an ND Tenax (ND-T), an ND Tenax/charcoal (ND-TC), an ST Tenax, and an ST Tenax/charcoal (ST-TC) trap and analyzed, the ST-TC trap would yield a much lower area response. The low response was probably related to the design of the ST traps and the Model 320 thermal desorption unit, which did not force the purge gas through the trap but allowed some of the gas to flow between the outside of the trap and the chamber wall. The difference in response is exemplified by the data for TCFM in Table 3-3, which were obtained between April 24 and 27, 1984.

TABLE 3-3. COMPARISON OF EXAMPLE CALIBRATION DATA FOR TCFM BETWEEN TRAP TYPES

Trap type	Amount, ng	Principal ion response, area units	Internal standard		Response factor, corrected for internal standard
			ng	Area response	
ST-T,ND-T,ND-TC	90	75,000-80,000	258	282,000-300,000	0.69-0.76
ST-TC	96	9,700	258	117,000	0.22

In general, the area response for ST-TC traps was approximately one-half of the area responses for the other three trap types. The calibration response factors, which are ratioed to the internal standard to account for system losses, also differed between the ST-TC and other trap types, vinyl chloride and trichlorofluoromethane. However, the response factors for chloroform, carbon tetrachloride, benzene, and tetrachloroethylene were not that much different between the trap types. These data suggest that some diffusion of the compounds (especially the more volatile ones) from the Tenax to the charcoal portion of the ST-TC trap is taking place in the desorption chamber. Once the compounds are adsorbed on the charcoal, the thermal desorption may not be efficient, which would result in low area responses.

A difference was not shown between calibration responses for the ND-T and ND-TC traps. The most likely explanation is two-fold: first, the purge flow is forced through the ND traps, and second, the calibration materials loaded onto the traps probably remain in the Tenax portion of both traps. (Unlike the ST-TC trap, the forced purge flow through the ND-TC trap would minimize the potential for diffusion of the compound to the charcoal portion.) Thus, the calibration curves for the different traps (ND-T and ND-TC) both represent the thermal desorption properties of Tenax. The thermal desorption properties of charcoal are not reflected in calibration curves generated using procedures specified in the protocol.

Because the calibration responses among ST-T, ND-T, and ND-TC trap types were similar, one calibration curve per target compound was used to represent all three traps, and a separate curve was used to represent the ST-TC traps. A three-point (minimum) calibration curve was generated at the beginning of each test week (either high- or low-range, as appropriate) for ST-TC traps. A second curve was generated for the other three trap types. A different trap type was used to generate the three-trap curve each week, but all three points in a given week's curve were made with one type of trap.

After a sorbent trap was loaded with calibration standards, the trap was desorbed and analyzed as a sample. The area responses of the characteristic ion of each analyte (target compound) and internal standard (IS) were tabulated with their respective amounts loaded. A response factor (RF) was calculated for each compound versus its internal standard by using Equation 3-1.

$$RF = A_s C_{is} / A_{is} C_s \quad \text{(Eq. 3-1)}$$

where A_s = area of the characteristic ion for the analyte to be measured

A_{is} = area of the characteristic ion for the internal standard

C_{is} = amount (ng) of the internal standard

C_s = amount (ng) of the volatile analyte in calibration standard

The characteristic ions used for each target and internal standard are listed in Table 3-4.

TABLE 3-4. CHARACTERISTIC IONS

Compound	Ion, m/e
Vinyl chloride	62
Trichlorofluoromethane	101
Chloroform	83
Carbon tetrachloride	117
Benzene	78
Tetrachloroethylene	166
D_6 Benzene (IS)	84
Hexafluorobenzene (IS)	186

Vinyl chloride and TCFM were referenced to the HFB internal standard; the other targets were referenced to d_6 Benzene. The decision regarding which internal standard to use as a reference was based on a preliminary comparison of response factors for each target, calculated by using both internal standards. The use of HFB as an IS yielded more repeatable response factors for VC and TCFM than did d_6 Benzene.

The protocol stated that an average RF could be used for quantitation if the three calibration-point RF's were constant; i.e., had a relative standard deviation (RSD) less than 10 percent. Alternatively, the protocol allowed generation of a calibration curve, but it did not specify whether it should be linear or quadratic-fit; or, if a linear fit is used, what criteria for linearity must be met. The type of calibration curve suggested in the protocol was a plot of A_s/A_{is} versus RF; however, we used a calibration curve of A_s versus RF because it was available as a part of the GC/MS software. A computer-generated quadratic-fit curve to the calibration points was used in the laboratory study for each target compound instead of a linear-fit plot, to depict instrument response more accurately.

The weekly calibration curves were updated on each working day by the analysis of one or more of the calibration standards. The daily check-point standard was added to the previous calibration data, and a revised curve was generated for that day's analysis. The ST-TC traps were always used for the ST-TC curves; however, the type of trap used to update the three-trap curve (ND-T, ND-TC, and ST-T) was varied each day to ensure representativeness.

The protocol states that the response of the daily check standard must be within ±25 percent of the initial calibration curve or new standards should be prepared and analyzed. The magnitude and schedule of the laboratory study did not allow this criterion to be followed to the letter; however, in the few instances when a daily check standard did not meet the ±25 percent criterion, the data were carefully evaluated to determine if the difference was instrument-related or standard-related. In some cases, the calibration check was repeated; in no case, was it judged necessary to remix a methanolic standard or to regenerate an entire curve. It should be noted that each separate vinyl chloride calibration consisted of a fresh aliquot of VC taken from the gas cylinder standard, and thus was a "remade" standard. The comparison of response was always made against the initial weekly curves, not the previous day's updated curve, so that any daily drift could be detected.

The protocol did not specify whether the daily check point should be added to the initial calibration curve or just used for comparison as described. We did add the daily data, and we recommend that the protocol be so revised. In this way, the effect of any shift in the curve will be averaged to minimize error. If a linear-fit curve is being used, we also recommend that the daily check be made at the midpoint of the curve; however, if a quadratic-fit curve is used, the daily check points should be varied to include the low and high points as well as midpoints. If only midpoint checks are made, the quadratic-fit curve would always pass through the original end points and simply flex in the middle range. In the laboratory study, we initially made only midpoint checks to update the quadratic-fit curves until we noticed this effect; thereafter, the check point levels were varied to include end points as well as midpoints.

Another aspect of the calibration concerns analysis of low-level samples or blanks when the GC/MS sensitivity has been adjusted for high-level samples. Although the MS analysis may yield an area response at very low levels, repeatability of that low-level area response probably will be poor. Also, quantitation of that area response may be biased (low or high) by distortion of the calibration curve between zero and the lowest calibration point. For example, quantitation of blank samples that might actually contain 20 ng may be outside the linear working range of an instrument calibrated at 500, 1500, and 2500 ng levels. Of course, a blank analysis yielding 20 ng would have no impact on a sample at 2000 ng, as the blank would be equivalent to only 1 percent of the sample, an error much less significant than the overall method error. If more accurate blank results are desired when high-level samples are being analyzed, however, alternate procedures should be used, such as calibrating with a separate low-level standard for analysis of blanks. The RF of this standard could be used for quantitation of the blanks instead of the entire calibration curve.

The protocol does not address the order of calibration standard analyses or whether one sorbent trap can be used over and over for standard loading and calibration. In this study, we found that carryover of residual target analytes can occur when high-level standards are followed by low-level standards. This was especially evident for ST-TC traps that were used repeatedly. The reason may be related to diffusion of material to the charcoal and subsequent poor desorption, which would cause some of the amount initially loaded on the trap to continue to appear in subsequent runs of the same trap. We recommend that calibration standards be run from low to high. Also, any trap that has been loaded with relatively high levels of standards should be thermally desorbed overnight before being used again as a standard or a blank.

Daily checks of calibration response factors made during the laboratory study are presented in Appendix C. Evaluation of these data suggests that the protocol criterion calling for a limit of ±25 percent difference between initial and daily check response factors should be changed. The criterion in Method 624, which is similar except for the sorbent trap desorption, sets a limit of ±10 percent between the initial calibration and daily checks. The VOST protocol criterion should be changed to ±15 percent, except for vinyl chloride, which should be ±20 percent. The data analysis justifying these limits is presented in Appendix C.

SECTION 4

RESULTS

This section presents the results of experiments described in Section 2. Subsection 4.1 presents the results of Runs Q1 through Q8 and W1 through W8 that were conducted to assess precision, accuracy, the effect of sample holding time, and a comparison between ND and ST trap types. A separate subsection (4.2) on blank evaluation results is followed by Subsection 4.3, results of the ruggedness tests, R1 through R8.

4.1 PRECISION, ACCURACY, AND SAMPLE HOLDING TIME

4.1.1 Sampling Data Summary

Eight quad runs, Q1 through Q8, were conducted on dry test gases; each run consisted of two ND sampling trains and two ST sampling trains. Eight additional runs, W1 through W8, were conducted on a wet test gas; each run consisted of two similar sampling trains, either ND or ST. All of these samples were collected at nominal VOST protocol conditions; i.e., 1-liter/min sampling rate and 20-liter sample volume. All samples were analyzed within one week of collection except for those in Runs Q4 and Q5, which were analyzed two weeks and five weeks after collection respectively, to determine the effect of sample holding time. Data for the generation of test gases were shown previously in Section 3. As indicated in Table 3-1, the 15-ppb test condition corresponds to concentrations between 42 and 108 ng/liter, depending on the target compound, and the 0.5-ppb condition corresponds to concentrations between 1.4 and 3.6 ng/liter.

Table 4-1 summarizes the sample collection data for these runs. Each sampling train was assigned a sample number as indicated in the table. Individual sample fractions (the Tenax trap, backup Tenax/charcoal trap, and any condensate) were identified by adding a suffix or trap number to the sample number. The sample number consisted of one letter designating the sampling locations, a two-digit number for the nominal POHC concentration, two letters for the trap configuration, and three numbers identifying the probe liner, sampling train position within the quad sample box, and the meter control unit used to collect the sample. When preceded by the run number, each sample number represented a unique sample. For example, Sample No. Q7L.5ST112 was collected during Quad Run Q7 in the mobile laboratory (L) at a test gas concentration of 0.5 ppb (.5) using ST traps, the No. 1 probe liner, the No. 1 position in the quad sample box, and Meter Control Unit No. 2. The particular combination of trap type and train components was rotated to avoid any inherent biases. As shown in the table, the sample time, sample volume, and average sampling rate were all within 10 percent of desired values, although the protocol does not have criteria for evaluating these parameters.

The average probe temperatures were all well above the moisture dewpoint for the wet runs. Because moisture is usually present in samples at a much higher level than any target compound, preventing moisture condensation in the probe should be more than adequate to assure that none of the VOST target compounds condense in the probe, even if they have somewhat higher boiling points than water. The vapor pressure of most volatile organic compounds should be sufficient at ≈100°C and the concentration low enough to keep the material in a vapor phase.

TABLE 4-1. SUMMARY OF SAMPLING TRAIN CONDITIONS FOR PRECISION AND ACCURACY RUNS

Date (1984) and time (24-h)	Run No.	Sample No.	Nominal conditions of known gas stream		Sampling conditions							
			POHC concentration, ppb	Moisture content, % by volume	Net sampling time, min	Metered sample volume, liters	Average sampling rate, liter/min	Average probe temperature, °C	Gas temperature at exit of primary condenser, °C		Maximum vacuum, in.Hg	Post-test leak rate, in.Hg/min
									Avg.	Max.		
5/9 1435	Q1	L15ND111	15	Dry	18.8	20.00	1.06	122	18.7	21.1	2.0	<0.1
		L15ND222			18.4	20.00	1.09	122	18.1	21.1	3.0	0.1
		L15ST333			19.9	20.04	1.06	122	19.2	19.4	<2.0	<0.1
		L15ST444			21.5	20.00	0.93	122	20.0	20.0	2.0	<0.1
5/9 1635	Q2	L15ST143	15	Dry	18.8	20.02	1.06	120	20.0	20.6	<2.0	<0.1
		L15ST234			20.0	18.88	0.94	120	19.4	20.0	<2.0	0.1
		L15ND321			20.0	19.66	0.98	120	18.3	18.9	0.0	<0.1
		L15ND412			20.0	19.04	0.95	120	18.1	18.3	0.0	0.1
5/9 1835	Q3	L15ND144	15	Dry	19.3	20.00	1.04	122	23.3	23.9	<2.0	0.1
		L15ST233			18.9	20.02	1.06	122	22.8	23.3	<2.0	<0.1
		L15ND322			20.7	20.00	0.97	121	23.0	23.9	0.0	<0.1
		L15ST411			20.6	20.00	0.97	121	23.0	23.9	0.0	<0.1
5/11 1615	Q4	L15ND143	15	Dry	19.0	20.04	1.05	121	11.8	13.9	<2.0	<0.1
		L15ND221			20.0	20.07	1.00	119	11.1	12.2	0.0	0.0
		L15ST334			19.6	20.06	1.02	121	11.7	14.4	0.0	<0.1
		L15ST412			20.0	20.03	1.00	121	8.9	10.0	0.0	0.0
5/11 1803	Q5	L15ND144	15	Dry	20.2	20.04	0.99	121	21.1	22.2	<2.0	0.0
		L15ND222			20.1	20.02	1.00	121	21.3	22.8	0.0	0.0
		L15ST333			19.2	20.08	1.05	121	21.3	22.2	0.0	0.0
		L15ST411			19.0	20.06	1.06	121	20.7	22.8	0.0	0.0
6/5 1100	Q6	L.5ND111	0.5	Dry	20.0	20.00	1.00	131	18.2	20.0	2.5	<0.1
		L.5ND222			20.0	20.00	1.00	131	18.2	20.0	2.0	<0.1
		L.5ST333			21.7	19.97	0.92	131	17.8	20.6	2.0	<0.1
		L.5ST444			20.8	20.00	0.96	131	17.8	20.6	2.5	<0.1
6/5 1407	Q7	L.5ST112	0.5	Dry	20.7	20.00	0.97	121	16.8	20.0	2.0	<0.1
		L.5ND221			20.3	20.00	0.98	121	16.8	20.0	2.0	<0.1
		L.5ST334			20.6	20.00	0.97	121	17.3	20.0	2.5	<0.1
		L.5ND443			19.8	20.03	1.01	121	17.3	20.0	3.2	<0.1
6/6 1050	Q8	L.5ST111	0.5	Dry	19.5	20.00	1.02	133	12.1	13.9	2.0	<0.1
		L.5ST222			20.6	20.00	0.97	133	12.1	13.9	2.0	<0.1
		L.5ND333			19.0	20.00	1.05	133	13.4	14.4	2.0	<0.1
		L.5ND444			19.0	20.00	1.05	133	12.9	13.9	2.5	<0.1

(continued)

TABLE 4-1 (continued)

			Nominal conditions of known gas stream		Sampling conditions							
Date (1984) and time (24-h)	Run No.	Sample No.	POHC concentration, ppb	Moisture content, % by volume	Net sampling time, min	Metered sample volume, liters	Average sampling rate, liter/min	Average probe temperature, °C	Gas temperature at exit of primary condenser, °C		Maximum vacuum, in.Hg	Post-test leak rate, in.Hg/min
									Avg.	Max.		
6/12 1111	W1	L15ND333 L15ND444	15	31.3	19.3 19.0	20.00 20.00	1.04 1.05	129 129	14.6 14.6	16.7 16.7	4.0 3.5	<0.1 <0.1
6/12 1412	W2	L15ST333 L15ST444	15	29.5	18.8 19.6	20.00 20.00	1.06 1.02	127 127	16.1 16.1	18.9 18.9	2.0 2.5	<0.1 <0.1
6/13 0900	W3	L15ST334 L15ST443	15	33.1	19.6 19.2	19.99 20.00	1.02 1.04	118 118	16.9 16.9	19.4 19.4	3.0 2.0	<0.1 <0.1
6/13 1108	W4	L15ND334 L15ND443	15	30.5	19.0 20.0	20.00 20.00	1.05 1.00	125 125	16.2 16.2	16.8 16.8	3.5 2.5	<0.1 <0.1
6/19 1043	W5	L.5ND333 L.5ND444	0.5	29.0	19.5 20.3	19.99 20.00	1.02 0.98	134 134	16.0 17.1	18.3 18.9	2.5 3.5	0.0 0.0
6/19 1325	W6	L.5ST333 L.5ST444	0.5	30.0	19.6 20.0	20.00 20.00	1.02 1.00	133 133	16.1 16.7	16.1 16.7	<2.0 2.5	<0.1 <0.1
6/19 1546	W7	L.5ST334 L.5ST443	0.5	31.0	20.3 19.6	20.00 20.00	0.98 1.02	134 134	17.6 16.8	16.3 17.2	2.5 <2.0	<0.1 0.0
6/20 0952	W8	L.5ND334 L.5ND443	0.5	35.0	20.4 19.7	20.00 20.00	0.98 1.02	132 132	14.6 15.6	16.1 17.2	4.5 2.5	<0.1 <0.1

Temperature measurements of the sample gas leaving the first condenser indicated that 14 of the 16 runs had average values less than the limit of 20°C, and the remaining two were less than 24°C. The small deviation did not seem to affect results. All post-test leak rates were within acceptable limits.

4.1.2 Laboratory Data Summary

Table 4-2 presents the GC/MS analysis results for each sample sorbent trap. Blank results are shown on a separate table. The unique trap identification numbers shown include the ND or ST designation, a "T" for the Tenax traps or a "TC" for the Tenax/charcoal backup traps, and the individual serial numbers etched on the traps. The amounts of target compounds shown for each trap were taken directly from the GC/MS quantitation lists for each analysis and summed to determine the total for a given sample. The percent of each target compound collected on the Tenax trap was calculated to evaluate the effectiveness of the Tenax trap in collecting the sample, or the potential for breakthrough.

Most of the analyses were performed in accordance with planned procedures; however, a few analyses incorporated slight modifications or were voided. The analysis of Trap No. ND-TC-20 (a backup Tenax/charcoal trap for one of the Run Q2 samples) was voided. After the trap was connected to the purge lines and placed into the desorber oven, the analyst inadvertently forgot to switch the three-way valves from the ST desorber to the ND desorber; thus, no purge gas was flowing through the trap as it was heated at 180°C for the 10-minute desorption period. An immediate repeat desorption and analysis was made on the trap before disconnecting it from the system, but the resultant internal standard responses indicated the sample integrity

TABLE 4-2. ANALYTICAL RESULTS FOR VOST PRECISION AND ACCURACY RUNS

Date (1984)	Run No.	Sample No.	Trap No.	Amount of species in sample: Vinyl chloride, ng per trap	Vinyl chloride, total ng	Vinyl chloride, % on Tenax	Trichloro-fluoromethane, ng per trap	Trichloro-fluoromethane, total ng	Trichloro-fluoromethane, % on Tenax	Chloroform, ng per trap	Chloroform, total ng	Chloroform, % on Tenax	Carbon tetrachloride, ng per trap	Carbon tetrachloride, total ng	Carbon tetrachloride, % on Tenax	Benzene, ng per trap	Benzene, total ng	Benzene, % on Tenax	Tetrachloro-ethylene (perc), ng per trap	Tetrachloro-ethylene (perc), total ng	Tetrachloro-ethylene (perc), % on Tenax
5/9	Q1	L15MD111	MD-T-147 MD-TC-128	25.0 589.9	614.9	4.1	690.3 601.2	1292	53.4	1412 0.0	1412	100	1843 1.9	1845	99.9	983.0 5.3	988.3	99.5	2151 9.8	2161	99.5
5/9	Q1	L15MD222	MD-T-113 MD-TC-43	16.1 686.7	702.8	2.3	357.7 795.0	1153	31.0	1428 1.9	1430	99.9	1244 289.8	1534	81.1	994.1 6.7	1001	99.4	2088 15.1	2103	99.3
5/9	Q1	L15ST333	ST-T-61 ST-TC-40	25.3 103.3	128.6	19.7	416.6 598.9	1016	41.0	1348 103.5	1452	92.8	1219 211.9	1431	85.2	999.9 43.8	1044	95.8	1972 125.2	2097	94.0
5/9	Q1	L15ST444	ST-T-47 ST-TC-45	33.4 61.9	95.3	35.0	510.9 658.8	1170	43.7	1325 120.3	1445	91.7	1294 211.5	1506	85.9	1029 38.4	1067	96.4	2344 62.6	2407	97.4
5/9	Q2	L15MD412	MD-T-11 MD-TC-48	38.4 821.9	860.3	4.5	553.0 971.8	1525	36.3	1844 335.3	2179	84.6	1868 515.2	2383	78.4	1585 56.2	1641	96.6	3499 25.4	3524	99.3
5/9	Q2	L15MD321	MD-T-149 MD-TC-20	34.4 a	34.4	N/A b	486.5 a	486.5	N/A	1374 a	1374	N/A	1359 a	1359	N/A	983.9 a	983.9	N/A	2134 a	2134	N/A
5/9	Q2	L15ST234	ST-T-110 ST-TC-70	30.8 65.5	96.4	32.0	529.0 511.5	1040	50.9	1445 40.5	1486	97.2	1385 155.3	1540	89.9	1019 14.9	1034	98.5	1984 87.2	2071	95.8
5/9	Q2	L15ST143	ST-T-30 ST-TC-142	11.6 71.0	82.6	14.0	350.3 427.8	778.1	45.0	1398 58.2	1456	96.0	1287 206.0	1493	86.2	979.6 17.9	997.5	98.2	1902 111.1	2013	94.5
5/9	Q3	L15MD144	MD-T-47 MD-TC-110	58.1 628.6	686.7	8.5	325.1 607.3	932.4	34.9	1122 327.3	1449	77.4	1098 390.9	1489	73.7	941.2 73.5	1015	92.7	2630 24.1	2654	99.1
5/9	Q3	L15MD322	MD-T-126 MD-TC-76	103.0 646.2	749.2	13.7	363.2 616.7	979.9	37.1	1472 6.5	1478	99.6	1411 299.3	1710	82.5	1030 5.3	1035	99.5	2638 1.6	2640	99.9
5/9	Q3	L15ST233	ST-T-108 ST-TC-135	134.9 16.2	151.1	89.3	281.8 349.8	631.6	44.6	1132 174.2	1306	86.7	1069 297.2	1366	78.2	965 59.9	1025	94.1	2588 103.6	2692	96.1
5/9	Q3	L15ST411	ST-T-111 ST-TC-43	24.8 30.9	55.7	44.5	354.1 439.4	793.5	44.6	1175 157.5	1332	88.2	1172 261.5	1434	81.7	938.7 54.2	992.9	94.5	2282 76.2	2358	96.8
5/11	Q4	L15MD221	MD-T-119 MD-TC-50	18.1 249.2	267.3	6.8	525.3 462.2	987.5	53.2	1148 222.1	1370	83.8	1041 487.2	1528	68.1	914.0 75.7	989.7	92.4	2212 20.8	2233	99.0
5/11	Q4	L15MD143	MD-T-2 MD-TC-82	8.5 315.7	324.2	2.6	509.2 355.0	864.2	58.9	1309 74.2	1383	94.6	1219 311.4	1530	79.7	1044 31.2	1075	97.1	2270 11.6	2281	99.5
5/11	Q4	L15ST412	ST-T-29 ST-TC-167	18.4 119.1	137.5	13.4	480.7 90.0	570.7	84.2	1026 156.3	1182	86.8	1044 266.7	1310	79.7	810.2 76.2	886.4	91.4	1859 164.3	2023	91.9
5/11	Q4	L15ST334	ST-T-4 ST-TC-21	17.9 128.3	146.2	12.2	587.5 55.8	643.3	91.3	1446 12.2	1458	99.2	1346 162	1508	89.2	966.1 9.7	975.8	99.0	1713 137	1850	92.6

(continued)

TABLE 4-2 (continued)

Date (1984)	Run No.	Sample No.	Trap No.	Amount of species in sample																	
				Vinyl chloride			Trichloro-fluoromethane			Chloroform			Carbon tetrachloride			Benzene			Tetrachloro-ethylene (perc)		
				ng per trap	total ng	% on Tenax	ng per trap	total ng	% on Tenax	ng per trap	total ng	% on Tenax	ng per trap	total ng	% on Tenax	ng per trap	total ng	% on Tenax	ng per trap	total ng	% on Tenax
6/12	Q5	L15ND144	ND-T-35 ND-TC-28	8.5 277.3	285.8	3.0	413.8 565.0	978.8	42.3	1191 96.6	1288	92.5	1118 432.6	1551	72.1	945.1 23.5	968.6	97.6	2151 15.8	2167	99.3
6/12	Q5	L15ND222	ND-T-63 ND-TC-94	3.7 125.0	128.7	2.9	432.9 520.9	953.8	45.4	1424 8.3	1432	99.4	1262 349.9	1612	78.3	970.1 19.2	989.3	98.1	2686 16.6	2703	99.4
6/12	Q5	L15ST333	ST-T-83 ST-TC-88	10.0 182.6	192.6	5.2	525.5 108.8	634.3	82.8	1356 31.7	1387	97.7	1236 164.1	1400	88.3	962.5 20.0	982.5	98.0	1834 161.7	1996	91.9
6/12	Q5	L15ST441	ST-T-22 ST-TC-16	5.8 49.8	55.6	10.4	427.7 83.8	511.5	83.6	1178 76.7	1255	93.9	1141 180.0	1321	86.4	901.5 60.0	961.5	93.8	2247 101.8	2349	95.7
6/5	Q6	L.SND111	ND-T-8 ND-TC-24	0.2 7.9	8.1	2.5	10.9 43.6	54.5	20.0	33.5 3.1	36.6	91.5	37.2 13.1	50.3	74.0	33.2 13.2	36.4	91.2	69.7 5.0	74.7	93.3
6/5	Q6	L.SND222	ND-T-135 ND-TC-109	0.7 10.4	11.1	6.3	9.2 57.8	67.0	13.7	32.2 3.1	35.3	91.2	36.8 12.6	49.4	74.5	58.4 24.9	83.3	70.1	64.7 10.4	75.1	86.2
6/5	Q6	L.SST333	ST-T-109^c ST-TC-1	ND^b 1.9	1.9	0	34.0 56.6	90.6	37.5	24.6 9.1	33.7	73.0	23.2 10.8	34.0	68.2	69.1 13.4	82.5	83.8	117.8 15.2	133.0	88.6
6/5	Q6	L.SST444	ST-T-33 ST-TC-139	0.3 1.6	1.9	15.8	17.1 18.6	35.7	47.9	32.3 5.9	38.2	84.6	37.1 7.2	44.3	83.7	30.7 8.1	38.8	79.1	53.6 10.2	63.8	84.0
6/5	Q7	L.SND443	ND-T-62 ND-TC-107	0.7 10.6	11.3	6.2	8.7 19.3	28.0	28.6	30.9 3.3	34.2	90.4	35.8 13.4	49.2	72.8	44.6 16.2	60.8	73.4	65.3 2.8	68.1	95.9
6/5	Q7	L.SND221	ND-T-44 ND-TC-34	1.7 13.4	15.1	11.3	9.3 14.7	24.0	38.8	34.6 3.4	38.0	91.1	39.1 12.4	51.5	75.9	65.4 3.8	69.2	94.5	64.6 2.8	67.4	95.8
6/5	Q7	L.SST334	ST-T-48 ST-TC-118	0.4 3.5	3.9	10.3	21.5 19.7	41.2	52.2	30.4 6.1	36.5	83.3	38.2 6.9	45.1	84.7	45.4 6.3	51.7	87.8	56.3 9.0	65.3	86.2
6/5	Q7	L.SST112	ST-T-20 ST-TC-54^d	0.7 21.2^d	21.9	3.2	22.9 41.7^d	64.6	35.4	27.5 11.3^d	38.8	70.9	36.8 4.1^d	40.9	90.0	27.4 23.0^d	50.4	54.4	55.2 19.3^d	74.5	74.1
6/6	Q8	L.SND444	ND-T-16 ND-TC-79	2.3 10.1	12.4	18.5	11.6 28.7	40.3	28.8	34.8 4.9	39.7	87.7	42.4 13.9	56.3	75.3	33.5 3.6	37.1	90.3	71.6 2.8	74.4	96.2
6/6	Q8	L.SND333	ND-T-67 ND-TC-120	0.7 11.6	12.3	5.7	13.6 33.0	46.6	29.2	35.0 3.9	38.9	90.0	44.7 17.8	62.5	71.5	41.5 7.3	48.8	85.0	70.5 2.8	73.3	96.2
6/6	Q8	L.SST222	ST-T-38 ST-TC-60	0.8 3.3	4.1	19.5	20.6 12.8	33.4	61.7	32.6 7.8	40.4	80.7	40.8 8.0	48.8	83.6	31.4 7.1	38.5	81.6	56.2 9.7	65.9	85.3
6/6	Q8	L.SST111	ST-T-137 ST-TC-82	1.0 3.4	4.4	22.7	20.8 14.7	35.5	58.6	35.2 7.3	42.5	82.8	40.9 10.2	51.1	80.0	30.3 5.7	36.0	84.2	58.8 6.2	65.0	90.5

(continued)

TABLE 4-2 (continued)

				Amount of species in sample																	
				Vinyl chloride			Trichloro-fluoromethane			Chloroform			Carbon tetrachloride			Benzene			Tetrachloro-ethylene (perc)		
Date (1984)	Run No.	Sample No.	Trap No.	ng per trap	total ng	% on Tenax	ng per trap	total ng	% on Tenax	ng per trap	total ng	% on Tenax	ng per trap	total ng	% on Tenax	ng per trap	total ng	% on Tenax	ng per trap	total ng	% on Tenax
6/14	W1	L15HD333	HD-T-89 HD-TC-71	8.2 368.0	376.2	2.2	436.9 807.3	1244	35.1	1439 8.1	1447	99.4	1226 437.8	1664	73.7	1039 11.5	1050	99.0	2833 23.0	2856	99.2
6/14	W1	L15HD444	HD-T-113 HD-TC-170	10.3 429.0	439.3	2.3	458.0 892.1	1350	33.9	1250 192.5	1442	86.7	1100 545.3	1645	66.9	979.0 42.5	1021	95.9	2840 24.6	2865	99.1
6/14	W2	L15ST333	ST-T-102 ST-TC-154	11.6 349.0	360.6	3.2	456.9 359.0	815.9	56.0	1295 81.8	1377	94.0	756.9 323.0	1080	70.1	976.3 14.7	991.0	98.5	2831 57.1	2888	98.0
6/14	W2	L15ST444	ST-T-105 ST-TC-116	7.3 342.5	349.8	2.1	385.9 178.3	564.2	68.4	1123 125.6	1249	89.9	796.7 204.4	1001	79.6	949.1 30.3	979.4	96.9	2702 74.9	2777	97.3
6/15	W3	L15ST334	ST-T-146 ST-TC-44	11.9 492.7	504.2	2.3	476.6 177.6	654.2	72.9	1284 70.9	1355	94.8	889.2 188.8	1078	82.5	996.0 28.2	1024	97.3	2580 68.9	2649	97.4
6/15	W3	L15ST443	ST-T-9 ST-TC-24	11.5 343.1	355.0	3.4	402.3 219.1	621.4	64.7	884.1 263.6	1148	77.0	768.1 267.9	1036	74.1	746.7 134.1	880.8	84.8	2411 205.2	2616	92.2
6/15	W4	L15HD443	HD-T-70 HD-TC-154	7.6 353.0	360.6	2.1	459.7 695.6	1155	42.9	1463 23.3	1486	98.4	1230 490.2	1720	71.5	1027 11.3	1038	98.9	2830 18.4	2848	99.4
6/15	W4	L15HD334	HD-T-64 HD-TC-163	8.7 412.7	421.4	2.1	436.0 883.3	1319	33.0	1380 9.0	1389	99.4	1202 564.3	1766	68.0	1014 13.2	1027	98.7	2697 19.5	2716	99.3
6/20	W5	L.5HD333	HD-T-36 HD-TC-155	0.2 9.0	9.2	2.2	12.9 27.8	40.7	31.7	38.5 4.1	42.6	90.4	39.8 16.0	55.8	71.3	34.8 6.8	41.6	83.7	67.5 2.7	70.2	96.2
6/20	W5	L.5HD444	HD-T-60 HD-TC-118	0.4 12.9	13.3	3.0	12.9 34.8	47.7	27.0	38.1 4.1	42.2	90.3	42.2 11.7	53.9	78.3	48.2 6.9	55.1	87.5	70.1 1.9	72.0	97.4
6/20	W6	L.5ST333	ST-T-14 ST-TC-53	0.4 5.4	5.8	6.9	10.8 19.6	30.4	35.5	26.5[e] 3.4[e]	29.9	88.6	19.5[e] 8.8[e]	28.3	68.9	35.8 7.6	43.4	82.5	56.7 5.6	62.3	91.0
6/20	W6	L.5ST444	ST-T-130 ST-TC-58	0.8 8.4	9.2	8.7	21.6 24.9	46.5	46.5	32.1 8.2	40.3	79.7	32.6 7.4	40.0	81.5	33.4 11.4	44.8	74.6	70.2 6.0	76.2	92.1
6/20	W7	L.5ST334	ST-T-31 ST-TC-98	0.6 6.0	6.6	9.1	21.3 22.6	43.9	48.5	25.7 11.2	36.9	69.6	18.7 8.8	27.5	68.0	26.4 8.6	35.0	75.4	59.1 8.4	67.5	87.6
6/20	W7	L.5ST443	ST-T-172 ST-TC-94	0.2 6.3	6.5	3.1	23.6 56.4	80.0	29.5	30.7 7.9	38.6	79.5	24.6 8.1	32.7	75.2	30.3 4.9	35.2	86.1	66.9 8.3	75.2	89.0
6/20	W8	L.5HD443	HD-T-179 HD-TC-193	- 11.0	11.0	0	13.5 51.8	65.3	20.7	37.2 3.6	40.8	91.2	49.3 11.9	61.2	80.6	29.1 8.0	37.1	78.4	78.9 4.4	83.3	94.7
6/20	W8	L.5HD334	HD-T-149 HD-TC-20	0.1 7.7	7.8	1.3	12.5 52.7	65.2	19.2	26.8 8.7	35.5	75.5	30.8 13.7	44.5	69.2	52.7 10.6	63.3	83.3	70.5 5.5	76.0	92.8

[a] Analysis void due to wrong valve position during desorption. The total is biased low.

[b] N/A = Not applicable; ND = None detected.

[c] Improper amount of internal standard was added prior to analysis; therefore, representative internal standard values were used to calculate species amount.

[d] Tube was in desorber 10 minutes without purge flow; therefore, analysis is considered invalid.

[e] MS filament flickering during mid-portion of run; however, chloroform and carbon tetrachloride quantitations seem reasonable.

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had been violated. This type of error would not usually occur because only one type of trap configuration (ND or ST) would be used in a given laboratory. In voiding the analysis of this trap, the corresponding total results of both traps for VC and TCFM also became void because a significant amount of these two compounds was generally found on the backup traps. Only VC and TCFM results for this train were voided; because the other targets are detected primarily on the Tenax traps, the totals for the other targets in this train are probably biased somewhat low (~10 percent) by excluding the backup trap. However, this was not considered to be significant.

The analysis of Trap No. ST-TC-54 (one of the backup traps for Run Q7) was similar to that just described in that no purge flow passed through the trap during its initial desorption period. In this case, the three-way valves connecting the ST and ND desorbers in parallel were in their correct positions, but the analyst neglected to push the purge flow switch. This type of error could happen in a typical situation. A followup desorption and analysis on the trap prior to removing it yielded results that were comparable to similar samples.

Trap No. ST-T-109 (one of the Tenax traps in Run Q6) was analyzed with the wrong amount of internal standard loaded onto the trap. Tabulated amounts were recalculated using average internal standard response data for other analyses that particular day and the current average calibration response factors.

Midway through the analysis of Trap No. ST-TC-53 (a Run W6 sample), the mass spectrometer filament flickered, which caused erratic fluctuations in the instrument response between scans that included chloroform and carbon tetrachloride. Quantitated results seemed unaffected. Analyses of other samples were generally uneventful.

As expected, most of the VC detected in a given sample was collected on the backup Tenax/charcoal traps. For the ND trap types the amount of VC on the Tenax trap averaged 5 percent of the total amount detected with a relative standard deviation (RSD) of 88 percent. The relative standard deviation was calculated by dividing the standard deviation by the mean and expressing the result in percent. For the ST traps the amount of VC on the Tenax averaged 17 percent with an RSD of 113 percent. For TCFM, the amount on ND Tenax traps averaged 35 percent of the total with an RSD of 33 percent, and the average amount on ST Tenax traps was 56 percent with an RSD of 31 percent. The higher percentages for the ST traps are deceiving because the amount of VC and TCFM in a given ST-TC trap was generally less than for a comparable ND-TC trap. Values for the wet runs were slightly lower than the overall values just presented by approximately 5 percent or less. For example the TCFM wet runs averaged 30 percent for the ND Tenax traps compared to 35 percent for both wet and dry runs.

The amount of CF detected on the Tenax traps averaged 92 and 87 percent for the ND and ST traps with corresponding RSD values of 8 and 9 percent, respectively. For CT the amount found on the ND Tenax traps averaged 76 percent with an RSD of 9 percent, whereas the average amount for ST traps was 81 percent with an RSD of 8 percent. CF and CT data for wet runs were essentially identical in the case of ND traps, and approximately 3 percent less for the ST traps.

Analysis data for benzene indicated the average amounts detected on the Tenax traps were 91 and 90 percent for the ND and ST traps, respectively. Corresponding RSD values were 9 and 8 percent. Wet data for both trap types were essentially the same. Data for perc indicated that an average of 97 percent was detected on the ND Tenax traps with an RSD of 3 percent. For the ST traps the amount of perc detected on the Tenax was 92 percent with an RSD of 4 percent. Wet data for both trap types were similar to the overall data.

For the amounts detected on the Tenax/charcoal backup traps, it was not possible to determine absolutely whether the material was in the Tenax portions or the charcoal portion of the trap; however, the percentage amounts on the front Tenax trap were useful in suggesting probable distributions of materials. The high percentage of CF, benzene, and perc collected on the front Tenax trap (>85) indicates that any amount collected in the backup trap would probably be retained in the Tenax portion. Data for carbon tetrachloride (~75 to 85 percent on front trap) do not support the same hypothesis as strongly; yet it seems that any amount collected on the charcoal portion would still be less than 10 percent of the total. Conversely, data for VC strongly suggest that Tenax is ineffective at the tested conditions for collecting VC, and that essentially all of the VC retained by the sampling train was in the charcoal. These results were as expected because of VC's very low boiling point (-12°C). Results for TCFM indicate that a significant portion of the total sample was collected in the charcoal portion of the backup trap.

Overall these results indicate clearly that, if the backup Tenax/charcoal trap were replaced with a Tenax trap similar to the front one, the VOST would have been as effective in collecting CF, CT, benzene, and perc, and would have been ineffective in collecting VC. Results for TCFM are inconclusive on this point.

4.1.3 Blank Data Summary

Blank samples were collected throughout the laboratory study. Field blanks (actually a misnomer because the tests were conducted in a mobile laboratory instead of a field test site) consisted of traps that were prepared and treated in the same way as sample traps, assembled in a sampling train, disassembled, and replaced into respective containers until analyzed as a blank sample. Trip blanks accompanied sample traps into the "field," but were not removed from their containers. Laboratory blanks were traps prepared for use that remained in the analytical laboratory at all times. A summary of the blank data is presented in Table 4-3, including the blanks for the ruggedness tests. The amount of target compound detected on each trap is shown as well as the corresponding total representative of a sample pair. The combined statistics at the end of the table present the mean ($\bar{x}$), standard deviation (σ), and percent relative standard deviation (% RSD) for each of the three types of blanks.

Very little VC or CT appeared in any of the blanks. All CF blank levels were less than 10 ng per pair of traps, and all but one pair had blank levels of perc less than 10 ng. Results for TCFM and benzene were variable to a high degree. Two of the higher TCFM blanks may have been biased by residual carryover from a preceding sample or calibration analysis. There was no explanation for the other high TCFM blank value (for Trap No. ST-TC 163). Three trap blanks had extremely high benzene levels: Traps No. ND-T 40, ST-TC 148, and ST-T 12. Although the analysis of ST-T 12 could have been biased by carryover, the preceding sample contained only approximately 250 ng benzene; therefore, carryover could not reasonably be responsible for the 192-ng blank value. The benzene blank for Trap ST-TC 148 appeared to be biased by an interferent that could not be identified. The peak shape of the EICP at m/e 78 (the primary ion of benzene) resembled that of benzene on the front side of the peak, but the back part of the peak was distorted and

TABLE 4-3. SUMMARY OF FIELD, TRIP, AND LABORATORY BLANK DATA

Applicable run Nos. (nominal test concentration)	Blank type	Trap No.	Vinyl chloride		Trichlorofluoromethane		Chloroform		Carbon tetrachloride		Benzene		Tetrachloroethylene (perc)	
			ng per trap	Total ng per pair	ng per trap	Total ng per pair	ng per trap	Total ng per pair	ng per trap	Total ng per pair	ng per trap	Total ng per pair	ng per trap	Total ng per pair
Q1-Q3 (15 ppb)	Field	ND-T-134	a	a	a	27.8	a	a	a	0.3	2.4	9.3	a	3.0
		ND-TC-22[b,c]	a		27.8		a		0.3		6.9		3.0	
		ST-T-75	a	a	a	a	a	a	a	a	3.1	3.1	a	
		ST-TC-136	a		a		a		a		a		a	
	Trip	ND-T-40	a	a	a	a	a	a	a	a	107.7	117.5	a	a
		ND-TC-51	a		a		a		a		9.8		a	
Q6-Q8 (0.5 ppb)	Field	ND-T-102	a	a	a	0.4	3.2	5.9	a	a	3.3	13.6	1.7	3.1
		ND-TC-88	a		0.4		2.7		a		10.3		1.4	
		ST-T-123	a	a	1.0	5.0	4.0	8.0	a	a	3.8	10.1	3.4	7.3
		ST-TC-101	a		4.0		4.0		a		6.3		3.9	
	Trip	ST-T67	a	1.0	1.2	8.7	3.5	8.0	a	a	4.5	84.9	2.2	4.9
		ST-TC-148	1.0		7.5		4.5		a		80.4[d]		2.7	
	Lab[e]	ST-T-12[c]	1.3	1.7	0.3	12.9	3.5	9.0	5.2	5.2	192.0	199.5	3.7	8.6
		ST-TC-152	0.4		12.6		5.5		a		7.5		4.9	
W1-W4 (15 ppb)	Field	ND-T-45	a	a	a	a	3.2	6.1	a	a	6.0	16.7	6.0	9.2
		ND-TC-7	a		a		2.9		a		10.7		3.2	
		ST-T-105	a	a	a	a	3.0	8.2	a	a	5.3	10.3	3.8	9.2
		ST-TC-136	a		a		5.2		a		5.0		5.4	
	Trip	ND-T-6	a	a	0.2	0.2	3.1	5.5	a	a	5.3	10.7	5.6	8.6
		ND-TC-172	a		a		2.4		a		5.4		3.0	
	Lab[f]	ND-T-186	a	a	a	a	4.1	8.3	a	a	6.3	27.2	1.7	3.1
		ND-TC-194	a		a		4.2		a		20.9		1.4	
W5-W8 (0.5 ppb)	Field	ND-T-151	a	a	a	a	4.0	7.7	a	a	4.8	10.8	1.2	2.3
		ND-TC-161	a		a		3.7		a		6.0		1.1	
		ST-T-201[c]	a	a	2.9	3.3	4.2	8.9	0.3	0.3	12.9	16.9	1.9	4.2
		ST-TC-75	a		0.4		4.7		a		4.0		2.3	
	Trip	ND-T-190	a	a	a	a	3.3	6.6	a	a	23.3	53.1	1.0	1.8
		ND-TC-129	a		a		3.3		a		29.8		0.8	
	Lab	ND-T-183	a	a	a	a	3.5	6.8	a	a	5.5	26.6	1.0	2.1
		ND-TC-160	a		a		3.3		a		21.1		1.1	

(continued)

TABLE 4-3 (continued)

Applicable run Nos. (nominal test concentration)	Blank type	Trap No.	Vinyl chloride		Trichloro-fluoromethane		Chloroform		Carbon tetrachloride		Benzene		Tetrachloro-ethylene (perc)	
			ng per trap	Total ng per pair	ng per trap	Total ng per pair	ng per trap	Total ng per pair	ng per trap	Total ng per pair	ng per trap	Total ng per pair	ng per trap	Total ng per pair
R1-R4 (15 ppb)	Field	ND-T-15	a		a		a		a		8.1		a	
		ND-TC-84	a	a	a	a	a	a	a	a	5.7	13.8	a	a
		ST-T-171	a		a		a		a		14.5		a	
		ST-TC-119	a	a	a	a	a	a	a	a	0.6	15.1	a	a
	Trip	ST-T-202[c]	4.5		a		3.9		a		7.3		14.3	
		ST-TC-141	a	4.5	a	a	a	3.9	a	a	7.9	15.2	19.0	33.3
	Lab	ST-T-79	0.3		a		4.1		a		5.2		3.4	
		ST-TC-97	a	0.3	a	a	3.5	7.6	a	a	2.3	7.5	3.3	6.7
R5-R8 (0.5 ppb)	Field	ND-T-27	a		0.8		3.8		0.2		4.2		1.7	
		ND-TC-124	a	a	0.3	1.1	4.1	7.9	a	0.2	14.8	19.0	1.6	3.3
		ST-T-41[c]	a		31.7		4.9		a		6.4		3.9	
		ST-TC-163	a	a	25.9	57.6	4.8	9.7	a	a	2.6	9.0	4.0	7.9
	Trip	ND-T-81[c]	a		a		3.1		a		2.5		2.1	
		ND-TC-69[c]	1.0	1.0	a	a	3.6	6.7	a	a	13.0	5.5	2.6	4.7
Combined statistics	Field	$\bar{x}$, ng		a		7.9		5.2		a		12.3		4.1
		σ, ng		a		17.5		4.0		a		4.4		3.5
		% RSD		a		222		77		a		36		85
	Trip	$\bar{x}$, ng		1.1		1.5		5.1		a		47.8		8.9
		σ, ng		1.7		3.5		2.9		a		45.8		12.3
		% RSD		155		223		57		a		96		138
	Lab	$\bar{x}$, ng		0.5		3.2		7.9		1.3		65.2		5.1
		σ, ng		0.8		6.5		0.9		2.6		90.0		3.0
		% RSD		160		203		11		200		138		59

[a] None detected.

[b] The trap was broken near one of the ferrules and would not pass the pretest leak check in the train. After repeated leak-check attempts, the trap was replaced and used as a field blank.

[c] Blank analysis followed a sample or calibration analysis and could be biased by residual carryover.

[d] The sample peak was not all benzene; however, the quantity of nonbenzene components could not be determined.

[e] Analyzed two weeks later than the samples.

[f] Analyzed one week later than the samples.

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obviously dissimilar to other benzene peaks. In the case of an interferent with the primary ion, the protocol suggests quantitation on a secondary ion; however, benzene's secondary ions are low in abundance and this is not practical. Based on a rough comparison to normal benzene peaks, the area of the suspect peak that was actually benzene was approximately one-third of the integrated total area, thereby representing about 25 ng benzene. There was no obvious explanation for the high ND-T 40 blank other than poor pretest conditioning or degradation of the Tenax.

Overall, the average blank levels for all compounds other than benzene were less than 10 ng per pair of traps. The blank results for benzene and perc were surprising in that the field blanks were lower than the trip blanks or laboratory blanks, even though the field blanks supposedly should have had the highest levels. Because this phenomenon could not be explained, no blank corrections were made to any of the samples.

It is possible that some of the blank values were the result of inconsistent trap conditioning. This is understandable given the large number of traps (ST and ND) handled on a mass production basis during this laboratory study. As explained in Section 3, the preparation procedures to be used for the field test program have yielded much more consistent results.

4.1.4 Concentration Data Summary

Table 4-4 presents the total target compound concentrations measured in each sample. The metered dry gas sample volume for each run is given in liters corrected to 20°C and 760 mmHg. Sample concentrations were calculated by dividing the total amount of target detected on the Tenax and Tenax/charcoal traps by the sample volume at standard conditions. Table 4-5 presents the recovery values for these samples in terms of percent of expected value (%

TABLE 4-4. MEASURED SAMPLE CONCENTRATIONS FOR PRECISION AND ACCURACY RUNS (ng/liter)

Date (1984)	Run No.	Sample No.	Sample volume, liters at STP[a]	Vinyl chloride	Trichloro-fluoro-methane	Chloroform	Carbon tetra-chloride	Benzene	Tetrachloro-ethylene (perc)
5/9	Q1	L15ND111	19.95	30.82	64.76	70.78	92.48	49.54	108.3
		L15ND222	19.79	35.51	58.26	72.26	77.51	50.58	106.3
		L15ST333	19.57	6.57	51.92	74.20	73.12	53.35	107.2
		L15ST444	19.67	4.84	59.48	73.46	76.56	54.24	122.4
5/9	Q2	L15ND412[b]	18.83	45.69	80.99	115.7	126.6	87.15	187.1
		L15ND321[c]	19.63	(1.75)[d]	(24.78)	69.99	69.23	50.12	108.7
		L15ST234	18.50	5.21	56.22	80.32	83.24	55.89	111.9
		L15ST143	19.41	4.26	40.09	75.01	76.92	51.15	103.7
5/9	Q3	L15ND144	19.56	35.11	47.67	74.08	76.12	51.89	135.7
		L15ND322	19.47	38.48	50.10	75.56	87.42	52.91	135.0
		L15ST411	19.66	2.83	40.36	67.75	72.94	50.50	119.9
		L15ST233	19.37	7.80	32.61	67.42	70.52	52.92	139.0
5/11	Q4	L15ND221	19.52	13.72	50.59	70.18	78.28	50.70	114.4
		L15ND143	19.41	16.70	44.52	71.25	78.82	55.38	117.5
		L15ST412	19.30	7.12	29.57	61.24	67.88	45.93	104.8
		L15ST334	19.64	7.44	32.75	74.24	76.78	49.68	94.2
5/11	Q5	L15ND144	19.46	14.69	50.30	66.16	79.67	49.77	111.3
		L15ND222	19.18	6.71	49.73	74.67	84.04	51.58	140.9
		L15ST333	19.29	9.98	32.88	71.93	72.60	50.93	103.5
		L15ST411	19.43	2.86	26.32	64.58	67.98	49.48	120.9
6/6	Q6	L.5ND111	19.59	0.41	2.78	1.87	2.57	1.86	3.81
		L.5ND222	19.40	0.57	3.45	1.82	2.55	4.29	3.87
		L.5ST333	19.49	0.10	4.65	1.73	1.74	4.23	6.82
		L.5ST411	19.72	0.10	1.81	1.94	2.25	1.97	3.24
6/6	Q7	L.5ND221	19.45	0.78	1.23	1.95	2.65	3.56	3.46
		L.5ND443	19.38	0.58	1.44	1.76	2.54	3.14	3.51
		L.5ST112	19.26	(1.14)	(3.35)	(2.01)	(2.12)	(2.62)	(3.87)
		L.5ST334	19.49	0.20	2.11	1.87	2.31	2.65	3.35
6/7	Q8	L.5ND333	19.63	0.63	2.37	1.98	3.18	2.48	3.73
		L.5ND444	19.78	0.63	2.04	2.01	2.85	1.88	3.76
		L.5ST111	19.70	0.22	1.80	2.16	2.59	1.83	3.30
		L.5ST222	19.52	0.21	1.71	2.07	2.50	1.97	3.38

(continued)

TABLE 4-4 (continued)

Date (1984)	Run No.	Sample No.	Sample volume, liters at STP[a]	Vinyl chloride	Trichloro-fluoro-methane	Chloroform	Carbon tetra-chloride	Benzene	Tetrachloro-ethylene (perc)
6/12	W1	L15ND333	19.62	19.17	63.41	73.76	84.81	53.52	145.6
		L15ND444	19.80	22.19	68.19	72.85	83.10	51.59	144.2
6/12	W2	L15ST333	19.48	18.51	41.88	70.67	55.44	50.87	148.3
		L15ST444	19.65	17.80	28.71	63.54	50.95	49.84	141.3
6/13	W3	L15ST334	19.79	25.48	33.06	68.47	54.48	51.75	133.9
		L15ST443	19.61	18.10	31.69	58.53	52.83	44.92	133.4
6/13	W4	L.5ND334	19.69	21.40	67.00	70.52	89.69	52.17	137.9
		L.5ND443	19.50	18.49	59.25	76.22	88.22	53.25	146.1
6/20	W5	L.5ND333	19.53	0.47	2.08	2.18	2.86	2.13	3.59
		L.5ND444	19.68	0.68	2.42	2.14	2.74	2.80	3.66
6/20	W6	L.5ST333	19.38	0.30	1.57	1.54	1.46	2.24	3.21
		L.5ST444	19.59	0.47	2.37	2.06	2.04	2.29	3.89
6/20	W7	L.5ST334	20.15	0.33	2.18	1.83	1.36	1.74	3.35
		L.5ST443	20.00	0.32	4.00	1.93	1.64	1.76	3.76
6/20	W8	L.5ND334	20.38	0.54	3.20	2.00	3.00	1.82	4.09
		L.5ND443	20.04	0.39	3.25	1.77	2.22	3.16	3.79

[a] Standard conditions are 20°C and 760 mmHg.

[b] High concentrations were unexplained.

[c] Concentration includes amount on Tenax tube only.

[d] Values in parentheses were invalid.

TABLE 4-5. RECOVERY VALUES FOR PRECISION AND ACCURACY RUNS (% EV)[a]

Date (1984)	Run No.	Sample No.	Vinyl chloride	Trichloro-fluoro-methane	Chloroform	Carbon tetra-chloride	Benzene	Tetrachloro-ethylene (perc)
5/9	Q1	L15ND111	36.3	76.3	103	96.0	100	100
		L15ND222	41.9	68.7	105	80.5	103	98.4
		L15ST333	7.7	61.2	108	75.9	108	99.3
		L15ST444	5.7	70.1	107	79.5	110	113
5/9	Q2	L15ND412[b]	107	96.2	167	131	176	173
		L15ND321[c]	(4.1)[d]	(29.4)	101	71.6	101	100
		L15ST234	12.2	66.8	116	86.1	113	103
		L15ST143	10.0	47.6	108	79.5	103	95.7
5/9	Q3	L15ND144	82.3	56.4	107	78.8	105	125
		L15ND322	90.2	59.3	109	90.5	107	125
		L15ST411	6.6	47.8	98.0	75.5	102	111
		L15ST233	18.3	38.6	97.6	73.0	107	128
5/11	Q4	L15ND221	32.4	60.3	102	81.6	103	106
		L15ND143	39.4	53.1	104	82.2	113	109
		L15ST412	16.8	35.3	89.3	70.8	93.5	97.5
		L15ST334	17.6	39.1	108	80.1	101	87.6
5/11	Q5	L15ND144	34.6	59.9	96.3	82.9	101	103
		L15ND222	15.8	59.3	109	87.5	105	131
		L15ST333	23.5	39.2	105	75.6	103	96.1
		L15ST411	6.7	31.4	94.0	70.8	101	112
6/6	Q6	L.5ND111	29.3	98.2	82.7	81.3	115	108
		L.5ND222	40.7	122	80.5	80.7	265	109
		L.5ST333	7.1	164	76.5	55.1	261	193
		L.5ST411	7.1	64.0	85.8	71.2	122	91.5
6/6	Q7	L.5ND221	54.9	43.6	84.8	82.3	216	95.8
		L.5ND443	40.8	51.1	76.5	78.9	190	97.2
		L.5ST112	(80.3)	(119)	(87.4)	(65.8)	(159)	(107)
		L.5ST334	14.1	74.8	81.3	71.7	161	92.8
6/7	Q8	L.5ND333	44.1	81.4	85.7	98.5	149	103
		L.5ND444	44.1	70.1	87.0	88.2	113	104
		L.5ST111	15.4	61.9	93.5	80.2	110	91.2
		L.5ST222	14.7	58.8	89.6	77.4	119	93.4

(continued)

TABLE 4-5 (continued)

Date (1984)	Run No.	Sample No.	Vinyl chloride	Trichlorofluoromethane	Chloroform	Carbon tetrachloride	Benzene	Tetrachloroethylene (perc)
6/12	W1	L15ND333	45.3	73.8	108	88.5	109	135
		L15ND444	52.4	79.3	106	86.7	105	134
6/12	W2	L15ST333	43.4	48.6	102	57.4	103	137
		L15ST444	41.7	33.3	92.0	52.7	101	130
6/13	W3	L15ST334	60.1	38.4	99.7	56.7	105	124
		L15ST443	42.7	36.8	85.2	55.0	91.3	124
6/13	W4	L15ND334	50.3	77.3	102	93.0	106	128
		L15ND443	43.4	68.4	111	91.5	108	135
6/20	W5	L.5ND333	33.6	73.2	96.0	89.9	131	101
		L.5ND444	48.6	85.2	94.3	86.2	172	103
6/20	W6	L.5ST333	21.6	55.7	68.4	46.3	139	90.9
		L.5ST444	33.8	84.0	91.6	64.8	142	110
6/20	W7	L.5ST334	23.6	77.0	81.0	43.0	107	94.4
		L.5ST443	22.9	141	85.4	51.9	109	106
6/20	W8	L.5ND334	38.6	113	88.1	94.3	112	115
		L.5ND443	27.9	114	78.0	69.8	194	106

[a] Percent of expected value is the measured concentration expressed as a percentage of the expected concentration.

[b] High values were unexplained.

[c] Value represents amount detected on Tenax tube only.

[d] Values in parentheses were invalid.

EV), which is the measured concentration expressed as a percent of the concentration of the target compound in the sampled gas stream (from Table 3-1).

No explanation could be found for the high results of Sample No. L15ND412 in Run Q2; however, the differences are thought to be related to the sampling portion of the test run instead of the analysis portion for two reasons. First, the internal standard responses for both the ND-T and ND-TC trap of the sample are similar to comparable samples. Secondly, the high results show up in both the Tenax and Tenax/charcoal traps, which suggests that the sorbents actually were exposed to a higher level of target compounds than the other trains. As described previously for the analytical data, the VC and TCFM results for Run Q2, Sample No. L15ND321, were voided because the analysis of the Tenax/charcoal trap that contains most of these two compounds was voided. Results for the other four compounds in this sample may be biased low by approximately 10 percent. The high VC value for Run Q5, Sample No. L15ND144, is probably related to the effect of sample holding time, as these samples were analyzed five weeks later than others. One of the samples in Run Q6, No. L.5ST333, had unusually high TCFM and perc values, but there was no apparent reason for them. Results for Sample No. L.5ST112 in Run Q7 were voided because the Tenax trap remained in the hot desorber oven for 10 minutes without purge flow.

The mean measured concentration, standard deviation, and RSD for each paired run (two sampling trains run simultaneously at the same conditions) are shown in Table 4-6. For a group of runs; e.g., Q1 through Q5, the ND data are presented first followed by the ST data. The relatively high standard deviations and corresponding RSD's for CF, CT, benzene, and perc for the ND trains in Run Q2 are biased high by the slightly low values for Sample No.

TABLE 4-6. SUMMARY OF PAIRED RUN DATA

Date (1984)	Run No.	Train	Vinyl chloride			Trichloro-fluoromethane			Chloroform			Carbon tetrachloride			Benzene			Tetrachloro-ethylene (perc)		
			$\bar{x}$ (ng/liter)	σ (ng/liter)	% RSD	$\bar{x}$ (ng/liter)	σ (ng/liter)	% RSD	$\bar{x}$ (ng/liter)	σ (ng/liter)	% RSD	$\bar{x}$ (ng/liter)	σ (ng/liter)	% RSD	$\bar{x}$ (ng/liter)	σ (ng/liter)	% RSD	$\bar{x}$ (ng/liter)	σ (ng/liter)	% RSD
5/9	Q1	ND	33.16	3.32	10.0	61.51	4.60	7.4	71.52	1.05	1.5	85.00	10.58	12.4	50.06	0.74	1.5	107.3	1.41	1.3
5/9	Q2	ND	45.69[a]	-	-	80.99[a]	-	-	92.84	32.32	34.8	97.92	40.57	41.4	68.64	26.18	38.1	147.9	55.44	37.5
5/9	Q3	ND	36.80	2.38	6.5	48.88	1.72	3.5	74.82	1.05	1.4	81.77	7.99	9.8	52.40	0.72	1.4	135.4	0.50	0.4
	Q1-3	ND	38.55[b]	2.89[c]	7.5[d]	63.79	3.47	6.3	79.73	18.68	23.4	88.23	24.64	27.9	57.03	15.12	26.5	130.2	32.02	24.6
5/11	Q4	ND	15.21	2.11	13.9	47.60	4.29	9.0	70.72	0.76	1.1	78.55	0.38	0.5	53.04	3.31	6.2	116.0	2.19	1.9
5/11	Q5	ND	10.70	5.64	52.7	50.02	0.40	0.8	70.42	6.02	8.5	81.86	3.09	3.8	50.68	1.28	2.5	126.1	20.93	16.6
5/9	Q1	ST	5.75	1.22	21.2	55.70	5.34	9.6	73.83	0.52	0.7	74.84	2.43	3.2	53.80	0.63	1.2	114.8	10.75	9.4
5/9	Q2	ST	4.74	0.67	14.1	48.16	11.40	23.7	77.66	3.75	4.8	80.08	4.47	5.6	53.52	3.35	6.2	107.8	5.80	5.4
5/9	Q3	ST	5.32	3.51	66.0	36.48	5.48	15.0	67.58	0.23	0.3	71.73	1.71	2.4	51.71	1.71	3.3	129.4	13.50	10.4
	Q1-3	ST	5.25	2.18	41.5	46.78	7.93	17.0	73.03	2.19	3.0	75.55	3.10	4.1	53.01	2.20	4.2	117.1	10.51	9.0
5/11	Q4	ST	7.28	0.23	3.2	31.16	2.25	7.2	67.74	9.19	13.6	72.33	6.29	8.7	47.80	2.65	5.5	99.50	7.50	7.5
5/11	Q5	ST	6.42	5.03	78.3	29.60	4.64	15.7	68.26	5.20	7.6	70.29	3.27	4.6	50.20	1.02	2.0	112.2	12.30	11.0
6/5	Q6	ND	0.49	0.11	22.4	3.12	0.47	15.1	1.84	0.04	2.2	2.56	0.01	0.4	3.08	1.72	55.8	3.84	0.04	1.1
6/5	Q7	ND	0.68	0.14	20.6	1.34	0.15	11.2	1.86	0.13	7.0	2.60	0.08	3.1	3.35	0.30	9.0	3.48	0.04	1.1
6/6	Q8	ND	0.63	0	0	2.20	0.23	10.4	2.00	0.02	1.0	3.02	0.23	7.6	2.18	0.42	19.3	3.74	0.02	0.5
	Q6-8	ND	0.60	0.10	16.7	2.22	0.16	7.2	1.90	0.08	4.2	2.73	0.14	5.2	2.87	1.04	36.1	3.69	0.03	0.9
6/5	Q6	ST	0.10	0	0	3.23	2.01	62.2	1.84	0.15	8.2	2.00	0.36	18.0	3.10	1.60	51.6	5.03	2.53	50.3
6/5	Q7	ST	0.20[a]	-	-	2.11[a]	-	-	1.87[a]	-	-	2.31[a]	-	-	2.65[a]	-	-	3.35[a]	-	-
6/6	Q8	ST	0.22	0.01	4.5	1.76	0.06	3.4	2.12	0.06	2.8	2.54	0.06	2.4	1.90	0.10	5.3	3.34	0.06	1.8
	Q6-8	ST	0.17	0.01	5.9	2.37	1.42	59.9	1.94	0.11	5.7	2.28	0.26	11.4	2.55	1.13	44.3	3.91	1.79	45.8

(continued)

TABLE 4-6 (continued)

Date (1984)	Run No.	Train	Vinyl chloride			Trichloro-fluoromethane			Chloroform			Carbon tetrachloride			Benzene			Tetrachloro-ethylene (perc)		
			$\bar{x}$ (ng/liter)	σ (ng/liter)	% RSD	$\bar{x}$ (ng/liter)	σ (ng/liter)	% RSD	$\bar{x}$ (ng/liter)	σ (ng/liter)	% RSD	$\bar{x}$ (ng/liter)	σ (ng/liter)	% RSD	$\bar{x}$ (ng/liter)	σ (ng/liter)	% RSD	$\bar{x}$ (ng/liter)	σ (ng/liter)	% RSD
6/12	W1	ND	20.68	2.14	10.3	66.80	3.38	5.1	73.30	0.64	0.9	83.96	1.21	1.4	52.56	1.36	2.6	144.9	0.99	0.7
6/13	W4	ND	19.94	2.06	10.3	63.12	5.48	8.7	73.37	4.03	5.5	88.96	1.04	1.2	52.71	0.76	1.4	142.0	5.80	4.1
	W1,4	ND	20.31	2.10	10.3	64.46	4.55	7.1	73.34	2.88	3.9	86.46	1.13	1.3	52.64	1.10	2.1	143.4	4.16	2.9
6/12	W2	ST	18.16	0.50	2.8	35.30	9.31	26.4	67.10	5.04	7.5	53.20	3.17	6.0	50.36	0.73	1.4	144.8	4.95	3.4
6/13	W3	ST	21.79	5.22	24.0	32.38	0.97	3.0	63.50	7.03	11.1	53.66	1.17	2.2	48.34	4.83	10.0	133.6	0.35	0.3
	W2,3	ST	19.98	3.71	18.6	33.84	6.62	17.6	65.30	6.12	9.4	53.43	2.39	4.5	49.35	3.45	7.0	139.2	3.51	2.5
6/19	W5	ND	0.58	0.15	25.9	2.25	0.24	10.7	2.16	0.03	1.4	2.80	0.08	2.8	2.46	0.47	19.1	3.62	0.05	1.4
6/20	W8	ND	0.46	0.11	23.9	3.22	0.04	1.2	1.88	0.16	8.5	2.61	0.55	21.1	2.49	0.95	38.2	3.94	0.21	5.3
	W5,8	ND	0.52	0.13	25.3	2.74	0.17	6.3	2.02	0.12	5.7	2.70	0.39	14.6	2.48	0.75	30.2	3.78	0.15	4.0
6/19	W6	ST	0.38	0.12	31.6	1.97	0.56	28.4	1.80	0.37	20.6	1.75	0.41	23.4	2.26	0.04	1.8	3.55	0.48	13.5
6/19	W7	ST	0.32	0.01	3.1	3.09	1.29	41.7	1.88	0.77	3.7	1.50	0.20	13.3	1.75	0.01	0.6	3.56	0.29	8.1
	W6,7	ST	0.36	0.09	25.0	2.53	0.99	39.3	1.84	0.27	14.5	1.62	0.32	19.9	2.00	0.03	1.4	3.56	0.40	11.1

[a] One value only.

[b] Combined mean is a simple average of grouped run means.

[c] Pooled standard deviation; i.e., $(\Sigma\sigma^2/n)^{\frac{1}{2}}$.

[d] Mean RSD equals the pooled standard deviation divided by the combined mean.

L15ND321 and the unexplained high values for its paired run. This set of data for the ND trains in Run Q2 appears to be an outlier, based on examination of other values in the table for high level test runs. None of the other RSD values for CF, CT, benzene, or perc in Runs Q1 through Q5 or W1 through W4 (the high level dry and wet runs) were greater than 17 percent in the case of the ND paired trains (for perc in Run Q5) or 14 percent in the case of the ST trains (for CF in Run Q4), compared to RSD's of 35 to 41 percent obtained for Run Q2. Because the low bias to Sample No. L15ND321 was considered small and no explanation was found for the high results of its paired run, Run Q2 was included in all subsequent evaluations for CF, CT, benzene, and perc.

The highest RSD values obtained for VC in the high level runs were 14 percent for paired ND trains (Run Q4) and 66 percent for paired ST trains (Run Q3). These RSD values corresponded to concentrations of 14 and 4 ng/liter, respectively. The ST RSD values seem high because the amounts of VC detected in the ST samples were generally much lower than the ND samples. For TCFM, the highest RSD values were 9 percent for ND trains (Run Q4) and 26 percent for ST trains (Run W2). Corresponding standard deviations were 4 and 9 ng/liter, respectively. Run Q5 results for VC and TCFM were excluded from the ranges just described because the samples were analyzed five weeks after collection as part of the sample holding time evaluation.

For VC in the low level runs (Q6 through Q8 and W5 through W8), the highest RSD value for ND paired trains was 26 percent and for ST trains, 32 percent, corresponding to standard deviations of 0.15 and 0.12 ng/liter, respectively. For TCFM, the maximum RSD values obtained were 15 percent and 62 percent for ND and ST trains, respectively. These RSD levels corresponded to concentrations of 0.47 and 2.0 ng/liter. Maximum RSD values for CF were 9 percent for ND trains (Run W8) and 21 percent for ST trains (Run W6), corresponding to concentrations of 0.16 and 0.37 ng/liter, respectively. For CT the highest RSD values were 21 percent for ND and 23 percent for ST trains, corresponding to standard deviations of 0.55 and 0.41 ng/liter, respectively. Benzene results were more erratic with maximum RSD values up to 56 and 52 percent for ND and ST trains, corresponding to concentrations of 1.7 and 1.6 ng/liter, respectively. These differences are probably related to variability in the blank levels of benzene, an inherent contaminant of Tenax. For benzene, only one of the ST pairs had an RSD greater than 10 percent, compared with four of the ND pairs. For perc, the maximum RSD value for ND trains was 5 percent corresponding to 0.21 ng/liter. Except for one of the ST pairs, which had an RSD value of 50 percent, the highest RSD for ST trains was 14 percent, corresponding to 0.48 ng/liter.

The concentration data were analyzed statistically as described in the following subsection.

4.1.5 Statistical Analysis

Analysis of Variance--

The analysis of variance (ANOVA) is a statistical method of analysis that is of great power and importance in the examination of experimental data. If a set of observations can be classified according to one or more criteria, then the total variation between individual observations can be broken up into components that can be attributed to the different criteria of classification. Three different sets of data were obtained for evaluation by ANOVA:

- Dry quad runs at a nominal target compound concentration of 15 ppb (Runs Q1-Q3).
- Dry quad runs at 0.5 ppb (Q6-Q8).
- Dry quad runs at 15 ppb with different sample holding times (Q1-Q3, Q4, Q5).

In the first two sets of data the effect of the type of sampling train (i.e., ND or ST) on observed results was evaluated. Within each data set all runs were collected under nearly identical conditions as exhibited by the consistency of the test gas generation system (refer to Table 3-1). Therefore, the effect of temporal variations in concentrations "seen" by the trains (i.e., the effect of the quad run) was expected to be negligible. Any effects due to the quad run would not have an impact on the ANOVA results in regard to train type because each quad run consisted of simultaneous ST and ND samples. The effect of the quad run would reflect variations in the operation of the test gas generation system including stability of the cylinder gas concentrations.

In the third data set the effect of holding time was evaluated. Because all samples within a quad run were held for the same time prior to analysis, the effect of holding time was equivalent to the effect of the quad run for this data set.

In the first two data sets, observed concentrations for a given target compound were analyzed by a two-way ANOVA based upon the model:

$$Y_{ijk} = \mu + Q_i + T_j + QT_{ij} + A_{k(ij)}$$

where

Y_{ijk} = measured concentration of target compound

μ = constant (overall mean)

Q_i = effect of quad, i = 1,2,3, random

T_j = effect of sampling train (ND or ST), j = 1,2, fixed

QT_{ij} = interaction between sampling trains and quad

$A_{k(ij)}$ = effect of replicate measurements for the j^{th} sampling train in the i^{th} quad

In the two-way ANOVA, the effect of interaction between the two principal factors (quad and sampling train type) was also examined. The last term, the effect of replicate measurements, is the "error" term and includes all other effects not specifically analyzed. Simplistically stated, the ANOVA compares the variance of each factor to the variance of the error term to determine statistical significance, taking into account the various degrees of freedom. In our ANOVA, the calculated F ratio of each factor was compared to Fisher's tabulated F statistic at the appropriate degrees of freedom at the 10 percent significance level. This means that, for any effect (i.e., difference in results attributed to a factor) that was classified "significant," there is a 10 percent probability that the observed difference was due to chance. As previously noted, the effect of the quad was not expected to be significant for the first two data sets (dry test gases), but the effect was included in the model so that the same model could be used for all data analyses.

To analyze the data set on sample holding time, the effect of the quad was replaced in the model with the effect of holding time, with j = 1, 2, or 3. In this model the effect of the sampling train was not expected to be significant. Because the data set included five quad runs instead of three for the base model, appropriate changes were made for degrees of freedom.

The calculation table for the ANOVA model and an example application are shown in the appendix. The required computations for the ANOVA were performed by a computer using the Statistical Package for the Social Sciences (SPSS), Version 8.0, September 1, 1980. Tabulated results of the ANOVA calculations for each target compound and data set are also included in the appendix.

Missing Values--

As previously shown in Table 4-4, two of the values reported for Run Q2, Sample No. L15ND321 and all of the values reported for Run Q7, Sample No. L.5ST112, have been identified as invalid. In order to maintain the proper balance in the data set for the ANOVA computations, a procedure described by Bennett and Franklin* was used to calculate new values for those presumed to be in error. An explanation of the method used to calculate missing values is included in Appendix A. In each case where a calculated value was used in the ANOVA, the number of degrees of freedom was reduced by one.

Testing Homogeneity of Variance--

Application of the ANOVA procedure to test a hypothesis is based upon the assumption that the data are normally distributed with a common variance σ^2. While some departure from normality will not significantly bias the results of ANOVA, it is important to determine whether or not the assumption of common variance is valid for the particular data set.

The assumption of common, or homogeneous, variance was tested using a statistic proposed by Bartlett.** Application of Bartlett's test is illustrated in the appendix.

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*Bennett, C. A., and N. L. Franklin. "Statistical Analysis in Chemistry and the Chemical Industry." John Wiley and Sons, New York. 1954. pp. 379-385.

**Snedecor, G. W., and W. A. Cochran. "Statistical Methods." The Iowa State University Press, Ames, Iowa. 6th ed. 1967. pp. 296-298.

t-Test--

The t-test was used to evaluate two sets of data:

- Wet paired runs at 15 ppb (W1-W4).
- Wet paired runs at 0.5 ppb (W5-W8).

The paired wet runs could not be analyzed statistically in the strict sense to determine the effect of sampling train type because the ST and ND samples were not collected simultaneously as they were during the quad runs. Any evaluation of the effect of train types would necessarily have to include the effect of temporal variations in concentrations seen by the trains. As exhibited by the consistent operation of the test gas generation system (refer to Tables 3-1 and 4-1), the difference between runs should have been small enough to allow comparison of train types. Although this could not be proved, it was assumed that between-run differences were small so the data sets could be evaluated.

Because each data set was relatively small and only the effect of train type was to be evaluated, a t-test was considered to be the most appropriate statistical test to use. In the t-test, a t-value was calculated for each target compound in the data set:

$$t = \frac{2\,(\bar{x}_1 - \bar{x}_2)}{(S_1^2 + S_2^2)^{\frac{1}{2}}}$$

where $\bar{x}_1$ = mean target compound concentration measured by ND train

$\bar{x}_2$ = mean target compound concentration measured by ST train

S_1^2 = variance of ND train data

S_2^2 = variance of ST train data

To determine if there was a significant difference between train types. the t-value calculated for each compound was compared to the Student's-t tabulated value at the appropriate degrees of freedom at the 10 percent significance level. For these data sets an F-test was used to test the assumption of common variances. The t-test data and F-test calculations are included in the appendix.

4.1.6 Comparison of Sampling Trains by Target Compound

A summary of the test data comparing results for the ND and ST types of sampling trains is presented in Table 4-7. Results for each of four data sets are shown separately by target compound and train type. Mean concentrations, standard deviations, and percent relative standard deviations (RSD) are the same as in Table 4-6, and thus do not include any of the data previously identified as invalid or calculated as missing values. Means are simple averages of paired run data; standard deviations are pooled from paired run data. The RSD values represent the pooled standard deviations expressed as a percent of the means. The expected value (EV) is the average concentration of the target compound in the sampled gas stream (from Table 3-1). The percent of expected value (% EV) is the mean measured concentration expressed as a percent of the expected value. The statistical significance of the difference between the results measured by the two types of sampling trains was determined by ANOVA for the dry test runs. The statistical significance of any difference between train types for the wet runs was determined by use of the t-test. Differences between train types were determined to be statistically significant if the respective test indicated there was less than a 10 percent probability the difference was due to chance.

TABLE 4-7. SUMMARY OF PRECISION, ACCURACY, AND TRAIN-TYPE COMPARISON RESULTS[a]

Nominal test conditions	Parameter	Vinyl chloride		Trichloro-fluoro-methane		Chloroform		Carbon tetra-chloride		Benzene		Tetrachloro-ethylene	
	Trap type	ND	ST	ND	ST	ND	ST	ND	ST	ND	ST	ND	ST
0.5 ppb, dry[b]	$\bar{x}$, ng/liter	0.60	0.17	2.22	2.37	1.90	1.94	2.72	2.28	2.87	2.55	3.69	3.91
	σ,[c] ng/liter	0.09	0.01	0.31	1.42	0.08	0.11	0.14	0.26	1.04	1.13	0.03	1.79
	% RSD[c]	15.0	5.9	13.9	55.9	4.2	5.7	5.1	11.4	36.2	44.3	0.8	45.8
	EV[d]	1.42		2.85		2.29		3.20		1.64		3.59	
	% EV[d]	42	12	78	83	83	85	85	71	175	155	103	109
Significant difference?[e]		Yes		No		No		Yes		No		No	
0.5 ppb, wet[f]	$\bar{x}$, ng/liter	0.53	0.36	2.74	2.53	2.02	1.84	2.71	1.63	2.48	2.01	3.79	3.55
	σ, ng/liter	0.13	0.09	0.17	1.0	0.12	0.27	0.39	0.32	0.75	0.03	0.15	0.40
	% RSD	24.5	25.0	6.2	39.5	5.9	14.7	14.4	19.6	30.2	1.5	4.0	11.3
	EV	1.40		2.83		2.26		3.17		1.62		3.55	
	% EV	38	26	97	89	89	81	85	51	153	124	107	100
Significant difference?[g]		Yes		No		No		Yes		No		No	
15 ppb, dry[h]	$\bar{x}$, ng/liter	38.55	5.25	63.79	46.78	79.73	73.03	88.23	75.55	57.03	53.01	130.2	117.1
	σ, ng/liter	2.89	2.18	3.47	7.93	18.68	2.19	24.64	3.10	15.12	2.20	32.02	10.51
	% RSD	7.5	41.5	6.3	17.0	23.4	3.0	27.9	4.1	26.5	4.2	24.6	9.0
	EV	42.53		84.25		68.86		96.31		49.35		108.0	
	% EV	91	12	76	56	116	106	92	78	116	107	121	108
Significant difference?[e]		Yes		Yes		No		No		No		No	
15 ppb, wet[i]	$\bar{x}$, ng/liter	20.32	19.98	64.47	33.84	73.34	65.31	86.46	53.43	52.64	49.35	143.4	139.2
	σ, ng/liter	2.10	3.71	4.55	6.62	2.89	6.12	1.13	2.39	1.10	3.45	4.16	3.51
	% RSD	10.3	18.6	7.1	19.6	3.9	9.4	1.3	4.5	2.1	7.0	2.9	2.5
	EV	42.50		86.22		68.81		96.24		49.32		107.9	
	% EV	48	47	75	39	107	95	90	56	107	100	133	129
Significant difference?[g]		No		Yes		Yes		Yes		No		No	

[a] Includes data from quad Runs Q1 through Q3 and Q6 through Q8 and paired Runs W1 through W8. No data are corrected for blank values.

[b] Quad Runs Q6 through Q8, including all data except Run Q7, Sample No. L.5ST112 values for all compounds.

[c] Standard and relative standard deviations are pooled from paired run data.

[d] EV is the average expected value for applicable runs taken from the summary table of dilution system data and expected concentrations in ng/liter; percent of expected value, % EV = ($\bar{x}$/EV) x 100.

[e] Difference between train types based on analysis of variance at 10% probability level.

[f] Paired Runs W5 through W8, including all data. The moisture content of the sampled gas stream was approximately 30%.

[g] Based on t-test statistic at 10% probability level, difference between train types.

[h] Quad Runs Q1 through Q3, including all data except Run Q2, Sample No. L15ND321 values for vinyl chloride and trichlorofluoromethane.

[i] Paired Runs W1 through W4, including all data. The moisture content of the sampled gas stream was approximately 30%.

Vinyl Chloride--

As discussed previously, two sample values were invalid and replaced with calculated values in order to perform the analyses of variance. Application of the estimation procedure yielded a value of 39.95 ng/liter to replace the reported value of 1.75 ng/liter for Run Q2, Sample L15ND321, and 0.24 ng/liter to replace the reported value of 1.14 ng/liter for Run Q7, Sample L.5ST112.

The results of the statistical tests showed that the difference between the vinyl chloride concentrations determined with the two types of sampling trains was statistically significant (ρ <0.10) for three of the four nominal test conditions. The difference between the two types of sampling trains was greatest for the dry test runs at 15 ppb based on the average concentrations (i.e., ND = 38.55 ng/liter and ST = 5.25 ng/liter). For the wet runs at 15 ppb the average results obtained with the two styles of sampling trains agreed quite well (i.e., ND = 20.32 ng/liter and ST = 19.98 ng/liter). Based upon the tests of variances (Bartlett's and F-tests), the assumption of common variance within each of the four nominal test conditions was not rejected.

An examination of the data at each test condition indicated that the ST sampling trains were ineffective in all cases. The maximum amount of VC recovered by use of the ST train was 60 percent of the expected value for one of the wet runs at 15 ppb. The range of recoveries for all tested conditions was from 6 to 60 percent EV for the ST trains and from 28 to 107 percent EV for the ND trains. Only the ND results at the 15 ppb dry test conditions were considered reasonable, with an average recovery of 91 percent EV. The presence of approximately 30 percent moisture in the test gas had a different effect on the two types of trains. For the 0.5 ppb test conditions the moisture had little effect on the ND results, but the apparent effect on the ST results was to improve the average recovery from 12 to 26 percent EV. For the 15 ppb test conditions a similar impact on the ST trains was observed in that the average recovery improved from 12 to 47 percent EV for the wet tests. The effect of moisture was definitely detrimental to the ND train results at 15 ppb in that the average recovery was decreased from 91 to 48 percent EV.

RSD values were used as estimates of precision. The best and worst RSD values were for the ST trains at dry test gas conditions; however, these values were considered nonrepresentative because of very low recoveries (~12 percent EV). Pooled precision values for the ND train type at each test condition ranged from 15 to 25 percent RSD at 0.5 ppb and from 7 to 10 percent RSD at 15 ppb. Pooled precision values for the ST type train at the wet test condition were 25 percent RSD at 0.5 ppb and 19 percent RSD at 15 ppb.

Trichlorofluoromethane--

The analysis of variance was performed using an estimated value of 69.12 ng/liter to replace the value of 24.78 ng/liter for Run Q2, Sample L15ND321, and a value of 1.64 ng/liter for the value of 3.35 for Run Q7, Sample L.5ST112.

The statistical tests showed a significant difference between the results determined with the two types of sampling trains for the high concentration of test gas (i.e., 15 ppb) for both wet and dry test gas conditions. In both cases the highest concentration of TCFM was reported for the ND sampling train. For the low concentration of the test gas (i.e., 0.5 ppb) the results reported for the two types of sampling trains agreed quite well (i.e., 2.22 and 2.37 ng/liter for the dry test gas, 2.74 and 2.53 ng/liter for the wet test gas).

Based upon the tests of variances, the assumption of common variance within each of the four nominal test conditions was rejected only for 0.5 ppb dry test gas. When the variances are not homogeneous, the ANOVA results may not be as valid. Inspection of the data set in question suggests that the value of 4.65 ng/liter reported for Run Q6, Sample L.5ST333, may be an outlier. As noted previously, this is the sample improperly loaded with internal standard. It should be noted that this sample also yielded results for benzene and perc that seemed to be outliers, but results for the other three targets were not unusual. If the suspect value of 4.65 ng/liter is excluded from the data set (for 0.5 ppb dry test gas), the means measured by the ND and ST trains would be 2.22 and 1.89 ng/liter, respectively, for a difference of ±8 percent from the average. This compares to a difference of ±3 percent from the average when the suspect value is included in the analysis. The statistical significance of the difference between the trains obtained by excluding the suspect value could not be determined because of the small amount of data remaining.

Examination of the TCFM data indicated that the presence of moisture in the test gas affected only the ST trains at the high concentration of target compounds (15 ppb). The average recovery by the ST trains was 56 percent EV for the dry test runs versus 39 percent EV for the wet runs at 15 ppb. Conversely the average recovery by the ND trains was approximately 75 percent EV for both wet and dry runs at 15 ppb, with a range of individual values between 56 and 96 percent EV. At the 0.5-ppb test gas concentration, the average recoveries for the ND trains were 78 and 97 percent EV at dry and wet conditions, respectively, compared to average recoveries by the ST trains of 83 and 89 percent EV at dry and wet conditions. The range of individual sample recoveries (at 0.5 ppb) ranged from 44 to 122 percent EV for the ND trains and from 56 to 164 percent EV for the ST trains. The 164 percent EV value corresponds to the suspect concentration of 4.65 ng/liter.

The precision of the pooled data in each of the four test conditions ranged from 6 to 14 percent RSD for the ND trains. Precision of the pooled ST data at 15 ppb was 17 and 20 percent RSD for the dry and wet test conditions, respectively. The precision of the pooled ST data at 0.5 ppb was 40 percent RSD for the wet runs and 60 percent RSD for the dry runs. If the suspect ST value (4.65 ng/liter) is excluded, the precision of the ST trains at dry conditions would be 3 percent RSD, represented by only one pair of samples because the other pair had an invalid result.

Chloroform--

An estimated value of 1.89 ng/liter was used to replace the value of 2.01 ng/liter for Run Q7, Sample L.5ST112, in the ANOVA.

The statistical analyses indicate that the difference between the measurements made by the two types of sampling trains was significant only for the 15 ppb wet gas. For this test condition the average concentration measured by the ND trains was 73.34 ng/liter compared with 65.31 ng/liter for the ST trains, for a difference of approximately 11 to 12 percent between the types of trains. Although the statistical comparison indicated the probability that this difference was due to chance was less than 5 percent, a difference of 12 percent does not seem significant when compared to overall results including other compounds.

Bartlett's test rejected the assumption of common variance for only the 15 ppb dry test gas. When the variances are not homogeneous, the ANOVA results may not be as valid. For this nominal test condition the reported value of 115.7 ng/liter for Run Q2, Sample L15ND412, appeared to be an outlier, but there was no valid argument for rejecting it. It should be noted that the indicated sample also yielded suspect results for all the target compounds. When Bartlett's test was repeated, excluding this value and its replicate, the assumption of common variance was not rejected. Exclusion of the value 115.7 ng/liter results in a mean of 72.11 ng/liter for the ND trains, instead of 79.73 ng/liter when it is included, which compares even better with the average of 73.03 ng/liter for the ST trains. Thus, no change in the significance of between-train comparisons would result by exclusion of the suspect value.

An examination of the data sets indicated the presence of moisture in the test gas did not affect results obtained by the use of either train type. At the nominal test condition of 0.5 ppb the individual train recoveries ranged from a low of 68 percent EV for one of the wet ST trains to a high of 96 percent EV by one of the wet ND trains. At the 15-ppb test condition the individual ND train recoveries ranged from 101 to 167 percent EV if the suspect value is included or up to 111 percent EV if it is excluded from the data set. Recovery values for the ST trains were similar, ranging from 85 to 116 percent EV. Again the lowest ST recovery value was obtained during one of the wet runs.

Precision of the pooled data sets at each condition for the ND trains varied between 4 and 23 percent RSD if the suspect ND value is included, or between 1.5 and 6 percent RSD if the value is excluded from the data set. Precision of the pooled data sets at each test condition for the ST trains varied between 3 and 15 percent RSD.

Carbon Tetrachloride--

The result reported for Run Q7, Sample L.5ST112, of 2.12 ng/liter was replaced with an estimated value of 2.19 ng/liter in order to perform the ANOVA calculations.

The statistical analyses indicated that the results reported for the ND trains were significantly higher than those reported for the ST trains at all of the nominal test conditions except the 15-ppb dry gas. The assumption of common variance within each of the four nominal test conditions was not rejected by the tests of variances. The results reported for Run Q2, Sample L15ND412, however, appeared to be an outlier because the value of 126.6 ng/liter was much higher than similar samples. In addition, the value of 69.23 ng/liter reported for its paired sample was known to be biased somewhat low because the value includes only the Tenax portion of the sample.

Exclusion of the data for the two referenced ND samples (Run Q2) would result in an average concentration of 83.39 ng/liter for the ND trains (instead of 88.23 ng/liter if the data are included) versus 75.55 ng/liter for the ST trains at the 15 ppb dry test gas condition.

An examination of the data sets indicated that the presence of approximately 30 percent moisture by volume in the test gas had no effect on the performance of the ND trains but definitely had an adverse effect on the performance of ST trains to measure CT concentrations. The average recovery for the ST trains was 71 percent EV for the 0.5 ppb dry test condition compared with 51 percent EV for the 0.5 ppb wet test condition. A similar decrease in average recovery for the ST trains was exhibited by the data at the 15 ppb test condition with 78 and 56 percent EV at dry and wet test conditions, respectively. Recovery values for individual ST samples ranged from 55 to 86 percent EV for the dry test runs and from 43 to 65 percent EV for the wet runs (including 0.5 and 15 ppb data). By comparison the average recoveries of the ND trains ranged from 85 to 92 percent EV among the four test conditions. Recovery values for individual ND samples ranged from 70 to 94 percent EV for the wet runs. If the suspect ND samples from Run Q2 are included, the ND recovery values for dry test gas conditions ranged from 72 to 131 percent EV; but if they are excluded, from 79 to 96 percent EV.

Precision of the pooled data sets at each test conditions for the ND trains ranged from 1 to 28 percent RSD if the suspect ND sample is included, or up to only 14 percent if it is excluded from the data. The precision of the pooled data sets at each test condition for the ST trains ranged from 4 to 20 percent RSD.

Benzene--

An estimated value of 3.06 ng/liter was used to replace the invalid value of 2.62 ng/liter reported for Run Q7, Sample L.5ST112, in order to perform the ANOVA calculations.

The statistical analyses determined that the difference between the results reported for the two types of sampling trains was not statistically significant at any of the four nominal test conditions. The assumption of common variance within each of the test conditions was rejected for the 15-ppb dry runs and the 0.5-ppb wet runs. The value of 87.15 ng/liter reported for Run Q2, Sample L15ND412, and 3.16 ng/liter reported for Run W8, Sample L.5ND443, appear to be outliers. No other valid reasons were known for rejecting the suspect data, although the bias for the low-level sample may be related to inherent benzene contamination. Exclusion of the suspect values results in the acceptance of the assumption of common variance within all of the data sets and probably would have no effect on the statistical analyses for train comparisons.

An examination of the data at each test condition indicated that the presence of moisture in the test gas may have had some effect on the results measured by each train type, but the differences between the dry and wet data were similar to the differences between train types (which were determined not to be significant).

The very high recovery values obtained by both train types at the 0.5-ppb test conditions may be related to inherent benzene contamination, either because of inconsistent pretest conditioning effects or because of degradation subsequent to conditioning. The overall average recovery at 0.5-ppb conditions was approximately 150 percent EV with individual sample values ranging from 113 to 265 percent EV for the ND dry runs, from 110 to 261 percent EV for the ST dry runs, from 112 to 194 percent EV for the ND wet runs, and from 107 to 142 percent EV for the ST wet runs. Average recoveries at the 15-ppb test conditions were not as high as those for the 0.5-ppb test gas and ranged from 100 to 116 percent EV. If the suspect value from Run Q2 is excluded from the data set, the recovery values of individual samples ranged from 91 to only 113 percent EV; however, if the value is included, the range increases to 176 percent EV. Except for the Run Q2 sample, results were quite similar for both train types.

The precision of the test results was also worse for the low-level tests than for the high-level tests. At 0.5 ppb the precision of the pooled data sets varied between 2 and 44 percent RSD. For the tests conducted at 15 ppb the pooled precision varied between 2 and 27 percent RSD, if the suspect data from Run Q2 is included, or if it is excluded, between 2 and 10 percent RSD.

Tetrachloroethylene--

An estimated value of 3.61 ng/liter was used in the ANOVA calculation to replace the value of 3.87 ng/liter reported for Run Q7, Sample L.5ST112.

The statistical tests showed that there was no significant difference between the tetrachloroethylene (perc) concentrations reported for the two types of sampling trains. Bartlett's test rejected the assumption of common variance for the reported values in both the 0.5 and 15 ppb dry gas test runs. For the 15 ppb dry gas test runs the reported value of 187.1 ng/liter for Run Q2, Sample L15ND412, is much higher than its replicate pair, and in fact it is much higher than any of the other values reported for the three quads at this test condition. There is no known reason to reject this value. Likewise the concentration of 6.82 ng/liter reported for Run Q7, Sample L.5ST333, far exceeds any of the other reported values for runs at the 0.5-ppb dry test gas condition. As previously mentioned, this is the sample improperly loaded with internal standard. Deletion of both of these values results in the Bartlett test not rejecting the assumption of common variance.

An examination of the data at each condition indicated the presence of moisture in the test gas did not affect the ability of either type of sampling train to measure concentrations of perc. The average recovery values were higher at the 15-ppb test conditions than at the 0.5-ppb test conditions, ranging from 108 to 133 percent EV and from 100 to 109 percent EV, respectively. Recovery values for individual sampling trains at the 0.5-ppb test conditions ranged from 91 to 193 percent EV if the suspected outlier is included or from 91 to 115 percent EV if it is excluded from the data set. For the runs conducted on the 15-ppb test gas, the recoveries of individual samples ranged from 96 to 173 percent EV (including the other suspected outlier) or up to 137 percent EV (excluding the suspect value).

Precision values excluding the two suspected outliers ranged from 1 to 11 percent RSD for the pooled data sets at 0.5 ppb and from 1 to 9 percent RSD for the pooled data sets at 15 ppb. Inclusion of the suspected outliers changes these ranges from 1 to 46 and from 3 to 25 percent RSD, respectively.

Summary--

An abbreviated summary of the precision and accuracy (recovery) results just described is presented in Table 4-8. Data for the ND and ST sampling trains were combined at each of the four test conditions when the difference between the train types was not determined to be statistically significant and the precisions were comparable. In addition, the data for wet and dry test conditions were examined to determine if any of the results were similar, and if so they were combined. Because statistical comparisons were not made between wet and dry test conditions, the results were combined simply to summarize the overall results obtained and were not meant to be statistically precise.

Results for each target compound are shown for both nominal test gas concentrations. Where the data for wet and dry conditions or for ND and ST trains are not pooled, an identifier next to the value describes what data are included. The accuracy of results is represented by percent recovery of expected values (% EV), and is not expressed as a difference between measured and expected values. To convert percent EV results into percent accuracy (or more correctly, percent relative error), 100 can be subtracted from the tabulated values. For example, the percent relative error for chloroform at 0.5 ppb is -15 percent and at 15 ppb, it is +7 percent. The tabulated percent EV's were calculated from the average of all the paired-run mean concentrations in the combined data set and the corresponding expected concentrations.

TABLE 4-8. COMBINED PRECISION AND ACCURACY RESULTS AT EACH TEST CONCENTRATION

Nominal test concentration	Vinyl chloride[a]		Trichloro-fluoromethane[a]		Chloroform[a]		Carbon tetrachloride[a]		Benzene[a]		Tetrachloro-ethylene[a]	
	% EV[b]	% RSD[c]	% EV[b]	% RSD[c]	% EV[b]	% RSD[c]	% EV[b]	% RSD[c]	% EV[b]	% RSD[c]	% EV[b]	% RSD[c]
0.5 ppb	40 17	21 (ND) 25 (ST)	86 85 86	35[d] 11 (ND) 50 (ST)	85	8	85 71 51	10 (ND) 11 (ST-D) 20 (ST-W)	155	35[e]	105	23[d]
15 ppb	91 12 47	8 (ND-D) 42 (ST-D) 15 (ND-W,ST-W)	75 56 39	6 (ND) 17 (ST-D) 20 (ST-W)	107	15[d,f]	86 78 56 90	18 (ND+)[g] 4 (ST-D) 5 (ST-W) 1 (ND-W)	108	16[d]	121	14[d]

[a] The (ND) means that the reported value includes dry and wet data for ND traps. Accordingly, (ST) includes dry and wet data for ST traps. If the value represents only dry or wet data, a "D" or "W" suffix is added, respectively. These identifications apply to both EV and RSD. If an identification is not shown, the value includes data for both types of traps, dry and wet conditions.

[b] Percent of expected value = $(\bar{X}/EV) \times 100$, where $\bar{X}$ is the simple average of applicable grouped run means, and EV is the average expected concentration in ng/liter for applicable runs taken from the summary table of dilution system data.

[c] Relative standard deviations are pooled from applicable paired run data: $\% \text{ RSD} = [(\Sigma\sigma^2/n)^{\frac{1}{2}}/\bar{X}] \times 100$.

[d] Although variances for dry data did not meet the test for homogeneity, the values were pooled to show overall results.

[e] Variances for wet data did not meet the homogeneity test.

[f] The ND and ST wet values are included because of their relatively close comparison, even though a statistically significant difference was indicated.

[g] No significant difference was indicated between the ND and ST dry data; therefore, the ST dry data (shown separately for comparison with ST wet data) are incorporated in this value.

The range of percent EV's for individual samples has been described previously in the subsections for each target compound. The RSD values are pooled from all of the paired samples that make up the corresponding data set. Results in Table 4-8 represent all of the data except for those previously identified as invalid. None of the suspected outliers have been excluded. Exclusion of the outliers would tend to show better results than those reported in the table, especially for precision.

As shown by the tabulated results, neither the ND or ST train was very good for measuring vinyl chloride, although use of the ND trains did yield reasonable results at the 15-ppb dry gas test condition. Both train types yielded similar results for TCFM at the 0.5-ppb level and for chloroform, benzene, and perc at both levels. The ND train was clearly superior to the ST train for carbon tetrachloride at both 0.5 and 15 ppb and for TCFM at 15 ppb.

In general the results were not surprising except for the clear superiority of the ND train over the ST train in measuring carbon tetrachloride (CT) concentrations, the effect of moisture on the ST train in measuring CT and 15-ppb concentrations of TCFM, and the puzzling difference in the effect of moisture on measuring VC depending on the train type.

The superiority of the ND train in measuring VC and TCFM, the more volatile compounds of those tested, was expected because the flow characteristics of the desorption gas through the trap sorbent bed are better for the ND traps than for the ST traps.

The high recoveries for benzene at the 0.5-ppb test condition could probably be improved by correcting for blank levels, but as described previously, the results of blank analyses were too inconsistent to apply them in a meaningful way.

In the cases where a statistically significant difference between the trains was indicated, the ND trains yielded the better results.

4.1.7 Effect of Sample Holding Time

All samples for quad Runs Q1, Q2, and Q3 were analyzed in the laboratory within less than one week after sample collection. Samples from quad Run Q4 were analyzed two weeks after sample collection and those from quad Run Q5 were analyzed five weeks after collection. All of these samples were collected during the same week of sampling and at the same nominal test conditions, 15-ppb concentration of target compounds in a dry gas stream. The test gas generation system operated at a high degree of consistency during these tests as demonstrated by the data previously presented in Table 3-1. The measured concentration data were analyzed statistically by ANOVA to determine if the difference between results obtained at the three sample holding times was significant. For example, the average concentration of VC for Run Q5 (5-week holding time) was compared with the average concentration of VC for Run Q4 (2-weeks holding time) and for Runs Q1, Q2, and Q3 (holding time less than 1 week). If the difference between the concentration was significant ($\rho < 0.10$), the effect of holding time was significant. A summary of the results of the analysis of the effect of holding time is presented in Table 4-9.

As shown in Table 4-9, the reported concentration of each target compound tended to decrease as the time was increased between sample collection and sample analysis. The value obtained for any compound on either trap type, except VC on ST traps, was the highest when analysis was completed within 1 week. This apparent effect of sample holding time was statistically significant ($\rho < 0.10$) for vinyl chloride and trichlorofluoromethane. For TCFM the effect held for both the ND and ST trains. For vinyl chloride, the decrease

TABLE 4-9. SUMMARY OF SAMPLE HOLDING TIME RESULTS[a]

Sample holding time[b] (weeks)	Parameter	Vinyl chloride		Trichloro-fluoromethane		Chloroform		Carbon tetrachloride		Benzene		Tetrachloro-ethylene	
	Trap type	ND	ST	ND	ST	ND	ST	ND	ST	ND	ST	ND	ST
-1[c]	$\bar{x}$[d] ng/liter	38.55	5.25	63.79	46.78	79.73	73.03	88.23	75.55	57.03	53.01	130.2	117.1
	σ[d], ng/liter	2.89	2.18	3.47	7.93	18.68	2.19	24.64	3.10	15.12	2.20	32.02	10.5
	% RSD[d]	7.5	41.5	6.3	17.0	23.4	3.0	27.9	4.1	26.5	4.2	24.6	9.0
2[e]	$\bar{x}$, ng/liter	15.21	7.28	47.56	31.16	70.72	67.74	75.55	72.33	53.04	47.80	116.0	99.5
	σ, ng/liter	2.11	0.23	4.29	2.25	0.76	9.19	0.38	6.29	3.31	2.65	2.19	7.50
	% RSD	13.9	3.2	9.0	7.2	1.1	13.6	0.5	8.7	6.2	5.5	1.9	7.5
Difference,[f] %		-61	39	-25	-33	-11	-7	-14	-4	-7	-10	-11	-15
5[g]	$\bar{x}$, ng/liter	10.70	6.42	50.02	29.60	70.42	68.26	81.86	70.29	50.68	50.20	126.1	112.2
	σ, ng/liter	5.64	5.03	0.40	4.64	6.02	5.20	3.09	3.27	1.28	1.07	20.93	12.30
	% RSD	52.7	78.3	0.8	15.7	8.5	7.6	3.8	4.7	2.5	2.0	16.6	11.0
Difference,[f] %		-72	22	-22	-37	-12	-7	-7	-7	-11	-5	-3	-4
Significant difference ?[h]		Yes[i]		Yes		No		No		No		No	

[a] All samples collected at a nominal target compound concentration of 15 ppb in a dry gas stream. All data were used from Runs Q1 through Q5 except for Run Q2, Sample No. L15ND321 values for vinyl chloride and trichlorofluoromethane. No data are corrected for blank values.

[b] Time between sample collection and analysis. All samples were stored in refrigerated cans containing charcoal.

[c] Runs Q1 through Q3.

[d] Standard and relative standard deviations are pooled from paired run data.

[e] Run Q4.

[f] Difference between mean concentrations at indicated holding time and initial values,

$$\% = \frac{\bar{x}i - \bar{x}\text{ initial}}{\bar{x}\text{ initial}} \times 100$$

[g] Run Q5.

[h] Difference between holding times based on analysis of variance at 10% probability.

[i] The effect of sample holding time is significant for the ND train but not for the ST train.

in concentration as the holding time increased was significant for the ND sampling train only. In contrast, there was essentially no change in the concentration of vinyl chloride with increased holding time for the ST sampling train. This disparity in behavior between train types for VC could not be explained, but it is similar to the effect moisture had on VC (as described in Subsection 4.1.6).

Bartlett's test rejected the assumption of common variance for chloroform, carbon tetrachloride, benzene, and tetrachloroethylene. In each case, however, the assumption of common variance was not rejected when the reported values for the apparent outlier (Run Q2, Sample L15ND412) were deleted. The determination that the effect of sample holding time was not significant for these four compounds would not be affected by deletion of the referenced values.

The 61-percent decrease in measured VC concentrations within two weeks of sample collection suggests that use of the ND train may not be practical for determination of VC concentrations. In any case, the sample should be analyzed immediately. Use of the ST train was ineffective for VC because of the very low recovery values (~12% EV as shown in Table 4-7).

For TCFM a decrease in concentration of approximately 25 percent within two weeks of collection for the ND trains also indicates that samples should be analyzed as soon as possible after collection. Again, the ST trains were not very effective because of low recovery (~56% EV as shown in Table 4-7). The similarity between results at the 2- and 5-week holding times seems to indicate that any significant loss of TCFM occurs within the first two weeks.

Results for the other four target compounds were similar. All average decreases from initial values were less than 15 percent. It should be noted that these results are for high level (~15 ppb), dry samples, which may be "ideal" samples. The effect of sample holding time should also be determined for actual field samples.

4.2 BLANK EVALUATION RESULTS

The results of the blank evaluation samples are given in Table 4-10. The blank sorbent traps were conditioned during the early stages of the laboratory study, set aside, and stored in the same manner as actual samples. Initially, a set of preliminary blank evaluation samples was analyzed by GC/MS to check the effectiveness of conditioning. The preliminary set consisted of two pairs (a pair consisted of one Tenax and one Tenax/charcoal trap) of each trap configuration (ND and ST). The blank evaluation sample set consisted of six additional pairs of each trap type, which were analyzed as follows: two pairs each of ND and ST traps initially, two pairs each two weeks later, and each of the remaining two pairs two weeks after that, or a total of four weeks later than the initial pairs. Analytical data were evaluated with respect to the presence of target compounds and also other species. Differences between ND and ST types, Tenax and Tenax/charcoal traps, and holding times were investigated. The target compounds in the blanks were quantitated in the same manner as samples; the other species were referenced to the internal standard in terms of area responses. Analyses of the blank traps were scheduled to coincide with weeks when the GC/MS was calibrated for low-level (0.5 ppb) samples to yield better quantitation of the targets and more sensitivity to the presence of other contaminants.

The results for the target compounds were generally very low. Carbon tetrachloride and trichlorofluoromethane were detected in less than 10 percent of the traps and then only in amounts of 1.5 ng or less. Because of the extremely low quantities of these two compounds that were detected, they were

TABLE 4-10. SUMMARY OF BLANK EVALUATION RESULTS

Trap type	Trap number	Time between conditioning and blank analysis, weeks	General species group data, normalized area units[a]				Target compounds,[b] nanograms			
			Methyl group	Ambient group	Others	Total	Vinyl chloride	Chloroform	Benzene	Tetrachloroethylene
ND-Tenax	ND-T-56[c]	0	d	d	d	d	e	0.1	4.2	0.8
	ND-T-138[c]	0	d	d	d	d	e	0.1	2.2	e
	ND-T-125	0	946	147	85	1,178	e	e	1.4	e
	ND-T-133	0	890	1,561	1,498[f]	3,949	e	e	1.4	e
	ND-T-127	2	2,406	1,246	35	3,687	2.0[g]	1.9[g]	3.4[g]	2.5[g]
	ND-T-25	2	1,042	630	110	1,782	e	1.6	3.0	1.4
	ND-T-106	4	181	279	76	536	e	2.9	4.2	1.5
	ND-T-139	4	4,362	1,472	1,006[h]	6,840	e	3.0	22.5	2.1
ND-Tenax/ charcoal	ND-TC-18[c]	0	d	d	d	d	e	0.1	2.0	e
	ND-TC-142[c]	0	d	d	d	d	e	e	2.1	e
	ND-TC-141	0	1,377	815	194	2,386	e	e	1.9	0.2
	ND-TC-105	0	1,422	1,454	460	3,336	e	e	1.8	e
	ND-TC-144	2	1,492	961	270	2,723	e	1.6	5.1	1.8
	ND-TC-46	2	1,016	1,027	268	2,311	e	1.5	6.6	1.6
	ND-TC-98	4	2,275	804	231	3,310	0.2	3.1	4.7	2.8
	ND-TC-87	4	4,712	995	408	6,115	1.0	3.0	6.5	3.0
ST-Tenax	ST-T-143[c]	0	d	d	d	d	e	0.3	2.9	e
	ST-T-128[c]	0	d	d	d	d	e	0.2	1.8	0.1
	ST-T-129	0	3,548	774	143	4,465	e	0.4	2.8	2.7
	ST-T-117	0	1,680	1,199	2,023[f]	4,902	e	0.1	1.9	e
	ST-T-114	2	15,205	2,066	402	17,613	2.5	2.4	13.5	3.4
	ST-T-122	2	2,678	1,189	66	3,933	1.4[g]	2.3[g]	4.9[g]	2.6[g]
	ST-T-112	4	1,352	738	102	2,192	1.4	5.0	5.5	4.3
	ST-T-63	4	200	3,522	98	3,820	e	3.5	4.3	2.5
ST-Tenax/ charcoal	ST-TC-71[c]	0	d	d	d	d	e	e	2.1	e
	ST-TC-17[c]	0	d	d	d	d	0.2	0.4	4.6	1.3
	ST-TC-127	0	18,519	861	407	19,787	0.6	0.2	4.0	e
	ST-TC-13	0	6,927	5,229	31,132[f]	43,288	e	0.4	9.0	e
	ST-TC-134	2	12,057	901	254	13,212	e	1.1	3.9	2.5
	ST-TC-124	2	3,304	667	74	4,045	e	1.1	2.7	0.5
	ST-TC-86	4	714	501	141	1,356	0.2	3.9	9.1	4.4
	ST-TC-5	4	642	529	106	1,277	e	3.4	5.2	4.0

[a] RIC area divided by thousand-area units of internal standard.

[b] Virtually no trichlorofluoromethane or carbon tetrachloride was found on any of the traps.

[c] Traps from preliminary blank evaluation.

[d] Undetermined.

[e] None detected.

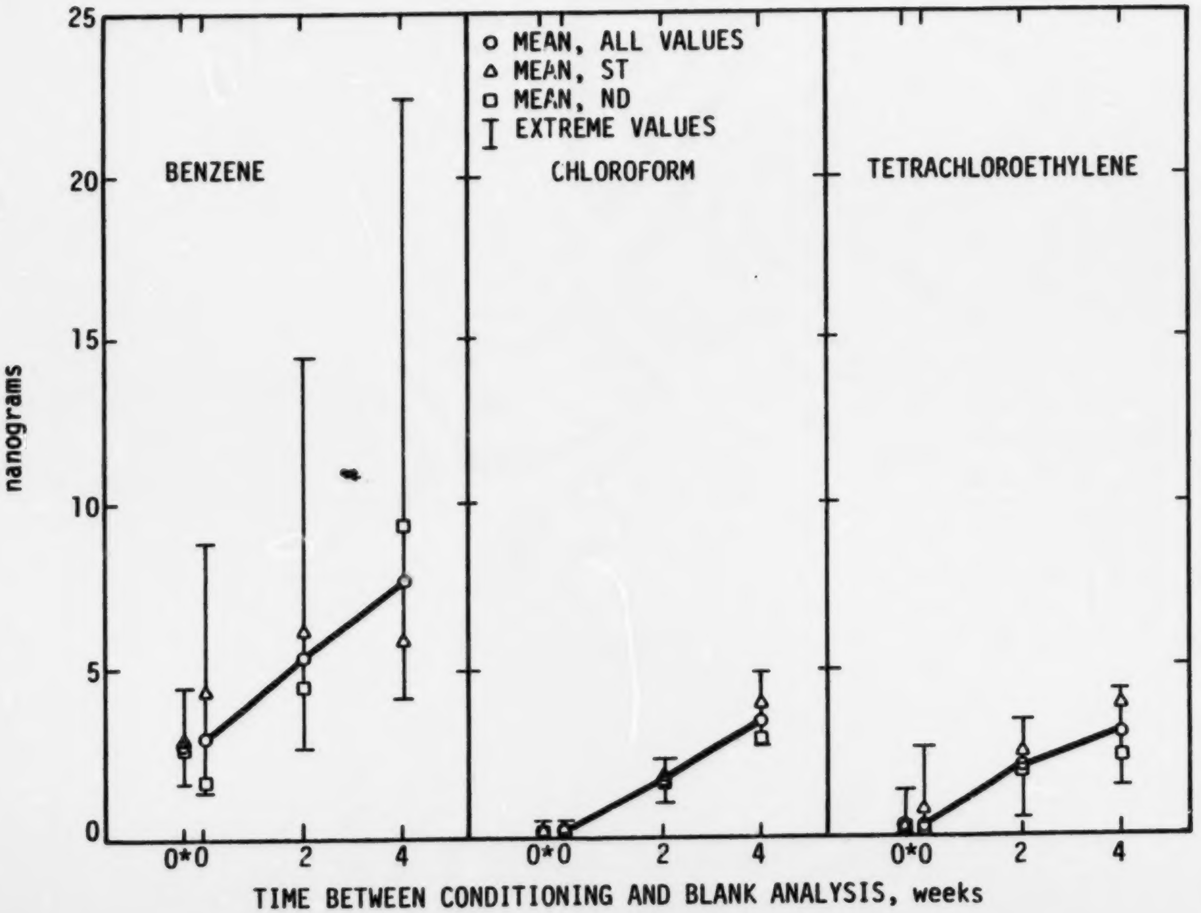
[f] May be related to carryover from a previous sample analysis.

[g] May be related to carryover from analysis of a previous calibration standard.

[h] Probably related to column bleed.

not considered for further comparative analyses. Based on an analysis of variance, there was no statistically significant difference (at a 10-percent probability level) between weeks 0, 2, and 4 for vinyl chloride. A statistically significant difference was shown in the data between weeks 0, 2, and 4 for chloroform, benzene, and tetrachloroethylene. The changes in weekly blank values for these three compounds are shown graphically in Figure 4-1. No effect was found due to either type of train (ND or ST) or trap (T or TC) type for vinyl chloride, carbon tetrachloride, or benzene. An effect due to train type was found for chloroform and tetrachloroethylene; that is, the ST traps had higher blank values than the ND traps, although the measured amounts of both compounds were quite low. For example, the highest amount of chloroform detected in a blank trap was 4.4 ng for the ST trap after four weeks. Similarly, for tetrachloroethylene the highest quantity found was 3.9 ng, also for an ST trap after four weeks. As noted in the table, some of the target compound results may be biased by carryover from a previous analysis of a calibration standard. These blank evaluation results indicate that conditioned traps may be stored for as long as four weeks with essentially no effect on sample concentrations, depending on the target compounds.

The results for other species in the blank traps were more difficult to interpret. The peaks of other species in the blank sample chromatograms were compared on the basis of area response from the reconstructed ion chromatograms (RIC) per 1000 area units for the two internal standards. The chromatograms of the blank samples were characterized by a large peak with a very early retention time that was identified as CO_2 and thus eliminated from further consideration. The compounds identified in the chromatograms were divided into three groups based on experience gained during this project with multiple desorptions of the same trap, analysis of room air samples, and a



* PRELIMINARY DATA

Figure 4-1. Plot of blank evaluation results for selected target compounds.

knowledge of the solvents used in our building. The first group consisted of five peaks at scans 50, 60, 72, 184, and 189. These peaks were tentatively identified as dimethylether, oxirane (or trinitromethane), methylformate, methylacetate, and dimethoxymethane, respectively. The compounds are listed as the "methyl" group in Table 4-10. The identification is only tentative as no ions with a mass to charge ratio (m/e) below 35 were acquired by the mass spectrometer because of the need to avoid an overwhelming peak due to the methyl alcohol solvent added with the internal standards.

The second group, listed as "ambient," consists of common solvents known to be used in the building. They are methylene chloride, acetone, carbon disulfide, isopropyl alcohol, trichlorotrifluoroethane (Refrigerant 113), and hexane. The last group is the sum of the remaining peaks and is listed as "other." Four compounds were frequently identified in this group--methylethylketone, pentane, 4-methyl-2-pentanone, and toluene. Generally this group represented less than 10 percent of the total RIC areas. The notable exceptions are footnoted in the table and are believed to be caused by the carry-over of heavy compounds from an earlier sample.

No correlation of the RIC data is apparent. There is a strong indication from other data comparisons that the "methyl" group contamination is associated with the charcoal. As previously noted in Section 3, the methanol extraction step in the preparation of charcoal has been eliminated and a significant reduction in contamination of this type has been achieved. Also, the new handling procedures developed for the ND type traps should significantly decrease the contaminants from the ambient air.

4.3 RUGGEDNESS TESTS

A series of tests (Runs R1 through R8) was conducted in accordance with Youden's approach* to determine if changes in selected variables had a significant impact on results obtained by the VOST method. Seven variables were tested at two levels in eight different combinations, which yielded a 1/16 replicate factorial experiment. Details of the procedures, variables, and results are presented in Appendix E.

In summary, the only solid conclusion that can be made from the ruggedness tests is that the trap configuration (ND or ST) significantly affects the measurement of carbon tetrachloride. This conclusion is supported by results of the precision and accuracy tests described in Section 4.1. Other than trap configuration for carbon tetrachloride, none of the variables was shown to have a definite effect on the VOST method. The data do indicate, however, that there may be an effect related to sample volume and/or sampling rate for measurement of TCFM, chloroform, and benzene. Recoveries for these compounds in the 5-liter samples were higher than recoveries for the 20-liter samples. When recoveries greater than 100 percent are considered, the 5-liter samples are probably magnifying the effect of any blank contamination or carryover in either the sampling or analysis.

A possible explanation for the inability to obtain any stronger conclusions from the ruggedness tests is that interactions cannot be evaluated. The fact that only one variable was shown to have a significant effect on only one compound is encouraging, however.

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*Statistical Manual of the Association of Official Analytical Chemists, Youden and Steiner, 1975.

SECTION 5

SUMMARY OF RESULTS AND CONCLUSIONS

5.1 PRECISION AND ACCURACY

The results of this laboratory test series indicate that the precision and accuracy of the VOST protocol depend on the target compound and on the type of sorbent trap used. In some cases, the precision and accuracy may also be affected by the moisture content of the sample stream and the amount of compound collected on the sorbent trap, which is a function of the concentration in the sample stream, the sampling rate, the sample volume, and the sampling time. Therefore, the precision and accuracy results are presented for each trap type and test condition where differences were shown. The effects of concentration, trap type, and moisture are then summarized.

The most obvious conclusion of the laboratory tests is that neither the tapered, necked-down (ND) type of sorbent trap design [referred to in the protocol as the inside-inside design (I/I)] nor the suspended-tube design (ST) of sorbent trap [referred to in the protocol as the inside/outside design (I/O)] produced acceptable results for vinyl chloride. The precision and accuracy tests indicated average vinyl chloride recoveries varying between 12 and 91 percent (see Table 4-8); however, the high value (91 percent by the ND traps for a 15-ppb dry gas stream) was not duplicated during the ruggedness test conducted at identical conditions. If the recovery value indicated by replicate samples in the ruggedness test is substituted for this high value, the range becomes 12 to 51 percent. Based on this range of values, the VOST protocol did not perform adequately in measuring vinyl chloride. This was expected because VC's boiling point (-12°C) is well outside the target range of the VOST protocol (∿30°-100°C).

The precision and accuracy for the ND and the ST types of sorbent traps varied in certain cases and are therefore discussed separately. For example, of the three compounds chloroform, carbon tetrachloride, and tetrachloroethylene, only carbon tetrachloride showed differences in precision and accuracy between the ND and ST traps. For carbon tetrachloride, the ST traps also showed differences between wet and dry conditions (see Table 4-8). The ND traps gave average recoveries of 85 and 86 percent for carbon tetrachloride at 0.5 ppb and 15 ppb respectively at both wet and dry test conditions. The precision reflected by the pooled relative standard deviation of the replicate pairs ranged between 10 and 20 percent. At 0.5 ppb, the ST traps gave average carbon tetrachloride recoveries of 71 and 51 percent during dry and wet conditions respectively, and the results were similar at 15 ppb. These results indicate that the ND traps were superior to the ST traps. The ND traps are less complicated in design and handling and have a positive forced flow during desorption; therefore, their performance should be as good as or superior to that of the ST traps for other, untested compounds.

The ND data for trichlorofluoromethane and carbon tetrachloride and all the data for chloroform and tetrachloroethylene indicate that average recoveries for the four compounds ranged from 75 to 121 percent, and the precision (expressed as the pooled RSD of the replicate pairs) varied between 8 and 23 percent at two different concentrations under both wet and dry conditions when approximately 50 ng or more of each compound was collected per sample.

Benzene results must be considered separately because of the inherent problem of benzene contamination in the Tenax sorbent. At concentrations of 15 or 0.5 ppb, no distinguishable effect was observed for trap type or moisture condition; however, the amount collected had a definite effect. Average benzene recoveries were 108 and 155 percent, with corresponding precision estimates of 16 and 35 percent, for collections of approximately 1000 and 50 ng respectively. During the ruggedness test, the average recovery for a single pair of trains was about 300 percent when the theoretical amount to be collected was 8 ng. Precision and accuracy results for benzene were not comparable to those for the other compounds when less than approximately 50 ng were collected in the sample.

With the possible exception of benzene, the estimates of accuracy obtained during this laboratory study (75 to 121 percent) were better than that given in the VOST Protocol (50 to 150 percent). The precision estimates (23 percent or better) are considered good. Because these estimates were obtained on a clean air matrix, they must be considered ideal. Additional precision and accuracy data need to be collected at an appropriate source (i.e., an incinerator).

5.1.1 Effect of Concentration

Although this project was not intended to determine whether concentration had any statistically significant effect on precision and accuracy, several conclusions can be made. The results for TCFM by the ND traps were essentially unaffected by concentration, but the ST trap results were affected. The average recovery for the ST traps was better at the lower concentration, but the precision was worse. It should be noted that the ST results for TCFM were also affected by moisture at the higher concentration, and the various effects are difficult to interpret individually.

Average recovery for chloroform and tetrachloroethylene was lower at the lower concentration, but the difference does not seem significant. Results for carbon tetrachloride were essentially unaffected.

Results for benzene were definitely affected by concentration, or more specifically, the amount of compound in the sample. At the lower concentration, the average recovery (155 percent) was much higher.

5.1.2 Effect of ND or ST Trap Type

Results for chloroform, benzene, and tetrachloroethylene were not significantly affected by trap type. The ND traps were clearly superior to the ST traps for TCFM and carbon tetrachloride, although the difference for carbon tetrachloride was most noticeable for the "wet" test conditions.

5.1.3 Effect of Moisture Content

Although it was not the intent of the project to determine if the moisture content in the sampled gas stream had a statistically significant effect on the VOST protocol, some conclusions are obvious. The ability of the ST traps to measure TCFM and carbon tetrachloride was definitely impaired by the presence of moisture.

5.2 RUGGEDNESS TEST RESULTS

The ruggedness tests supported the conclusion that the ND traps are superior to the ST traps for measurement of carbon tetrachloride. Otherwise, none of the seven variables was shown to have a definite effect on the VOST protocol. The results did confirm that recoveries of benzene can be much higher than theoretically possible when less than ~50 ng of benzene is collected in the sample.

5.3 SAMPLE HOLDING TIME

A trend toward lower recoveries with prolonged holding times was observed for all compounds included in this study. Excluding vinyl chloride, the only compound for which the lower recovery could be considered significant was trichlorofluoromethane, which showed approximately a 30 percent decrease on both types of traps when samples were analyzed 2 weeks after collection. Again, these results must be considered ideal because they were obtained on a matrix of clean dry air; tests must be run on a more appropriate source matrix. Maintaining as short a period as possible between sampling and analysis may be important for some compounds.

5.4 BLANK EVALUATION

The blank evaluation study showed very low levels of all the target compounds except benzene, for which the results were generally higher and much more variable. Nevertheless, the average benzene blank level was less than approximately 16 ng per pair of sorbent traps, even after 4 weeks of storage. Careful review of the data and the records on the order of sample analysis led to the discovery that much of the other contamination shown in the blank evaluation study was due to the methanol extraction of the charcoal. Procedural changes have been recommended to eliminate this problem. Also, sample handling procedures were devised that significantly reduced (practically eliminated) ambient air contaminants. The hope is that these procedures will reduce contamination of field and trip blanks in the field study, as contamination of field blanks has been a significant problem with the VOST.

Overall, the blank evaluation study showed that conditioned traps may be stored for as long as 4 weeks prior to sampling with essentially no effect on the results.

5.5 ASSESSMENT OF BREAKTHROUGH

A secondary objective was to assess the breakthrough potential of the target compounds from the front Tenax trap to the backup Tenax/charcoal trap. This assessment was made by analyzing each sorbent trap in a sample individually and calculating the percentage of each target collected on the front trap.

As expected, virtually all of the VC detected in a sample was found on the Tenax/charcoal trap. Amounts of TCFM, CF, CT, benzene, and perc found on the ND Tenax traps averaged 35, 92, 76, 91, and 97 percent, respectively, of the total collected. A higher percentage of TCFM was detected on the ST traps, but these results are deceiving because the overall recovery of TCFM was generally less on the ST traps. Otherwise, the percentage amounts found on the ST Tenax traps were within ±5 percent of the ND results.

It was not possible to determine whether the target compounds found on the backup Tenax/charcoal traps were in the Tenax portion or the charcoal portion; however, the percentages found on the front Tenax traps support the following conclusions:

- All the CF, benzene, and perc is retained in the Tenax.
- A small amount of CT (probably less than 10 percent of the total sample) may pass through to the charcoal.
- Virtually none of the VC is retained by the Tenax.
- A significant but unknown portion of TCFM passes through to the charcoal.
- If the backup Tenax/charcoal trap is replaced with a Tenax trap similar to the front one, the VOST would be as effective in collecting CF, CT, benzene, and perc but not as effective for VC, and results are inconclusive for TCFM.

5.6 PROCEDURAL RECOMMENDATIONS

During the course of this laboratory study, careful attention was given to sampling, analytical, and quality control procedures. The following summaries of recommendations for modifications to the protocol are described in Section 3 and Appendices B, C, and D:

- Calibration procedure for the dry gas meter--A valid procedure does not currently exist for verifying the accuracy of the dry gas meter at sampling rates less than 1 liter/min. It is recommended that a bubble-meter approach be used, but it needs to be validated.
- Field blank handling--The trap storage containers should be purged with nitrogen gas.
- Substitution of methanol instead of pentane for extraction of glass wool used in packing the sorbent traps--This would eliminate residual pentane after extraction and the need to check for it.
- Elimination of methanol extraction of charcoal--The extraction step may not be necessary and can make pretest blank checks worse.
- Prescreening of charcoal prior to its use in traps--Each lot of charcoal should be screened by blank checking it in a sorbent trap. If it fails, the charcoal can be preheated in a vacuum oven or extracted with methanol.
- Prescreening of each lot of Tenax--It is recommended that a small portion of each new batch of Tenax be extracted, conditioned, and blank-checked to assure that it is acceptable prior to packing a large quantity of sorbent traps.
- Predrying of Tenax before it is placed in the vacuum oven--The methanol-extracted resin should be partially dried under an infrared lamp to prevent splattering of the Tenax due to boiling residual methanol.
- More specific procedures for ND sorbent trap conditioning to enhance consistency of blank levels--A 28-hour conditioning period is recommended along with detailed procedures designed to maintain a positive purge flow during heating and cooling and to minimize ambient contamination.
- More sensitive and specific calibration procedures for blank checking--It is recommended that a quantitative method such as the cryogenic trapping method be used to conduct a pretest blank check on each pair of traps. Specific target compounds should be included when possible in the blank check calibration as well as benzene and toluene. Instrument sensitivity should be set to produce a response

of at least 40 percent of scale for ~20 ng of benzene. Specific steps are included to minimize contamination of the traps following the blank check.

- Quality control for blank checking--A system blank is recommended each day and a recovery check every week.
- Different sample desorption flow rate consistent with Method 624--40 ml/min is recommended instead of 100 ml/min.
- Development of a procedure for evaluating performance of the analytical trap in the purge and trap apparatus--Different traps can be evaluated by conducting system recovery checks that purposely bypass the purge vessel.
- Addition of a recovery check procedure for the GC/MS analytical system--A weekly recovery check is recommended for comparison of raw area responses for an on-column injection with those for a normal sample trap calibration.
- Recommended procedure for determining acceptable analytical separation to assist in column selection and other GC conditions--It is recommended that alternate GC columns be permitted and a criteria for evaluating them be specified, such as the one in EPA Method 624, Section 12.2, for resolving structural isomers.
- Recommended procedures for determining appropriate calibration levels--One or more preliminary samples can be collected and analyzed prior to calibration so that instrument sensitivity and calibration standards can be adjusted to suit the actual target level in the samples.
- Recommended specific daily calibration check procedures--The level of the daily check point should be varied if a quadratic-fit curve is used, and the mid-point should be used for a linear-fit curve. Also, it is recommended that the daily check point be used to update the curve. The daily check criteria should be reduced from ±25 percent to ±15 percent (except for vinyl chloride).

Overall, the laboratory evaluation accomplished all of its stated objectives. In addition, a number of discrepancies in the written protocol were identified and corrected.

5.7 RECOMMENDATIONS FOR FIELD TEST

The results of the laboratory phase (Phase I) of the VOST Protocol Validation indicated that the protocol is capable of yielding values of acceptable precision and accuracy on selected compounds under ideal laboratory conditions. The precision and accuracy of the protocol now must be assessed under field test conditions to substantiate its effectiveness in a source gas matrix (incinerator stack gas). The Phase I results have been incorporated in the planning of the field testing phase (Phase II), at a selected hazardous waste incinerator. Because the ND sorbent trap design yielded results as good as or better than the ST design, only the ND sorbent trap will be included in the field testing program. Also, to reduce the number of analyses, the front and backup sorbent traps for each sample will be analyzed simultaneously. The five volatile organic compounds recommended for the field testing are benzene, chloroform, carbon tetrachloride, tetrachloroethylene, and trichlorofluoromethane. Vinyl chloride (VC) is excluded because Phase I demonstrated the general ineffectiveness of the VOST Protocol in measuring VC.

If possible, the use of a sample-train spiking approach is recommended in Phase II to achieve the desired amount of target compound in the samples. This will permit determination of both accuracy and precision.

Except for benzene, the results of Phase I were similar for the five target compounds at both concentration levels tested; therefore, only one concentration of the target compounds is recommended for evaluation during the field testing. Because the inherent blank levels of benzene caused benzene recoveries at the low concentration of the test gas in Phase I to be biased on the high side, the concentration for Phase II should be high enough to minimize the effect of problems associated with benzene. A concentration equivalent to approximately 200 ng or more of each target compound in a sample is recommended (assuming the front and backup sorbent traps are analyzed simultaneously).

5.8 RECOMMENDATIONS FOR FUTURE WORK

The scope of the recommended field test project will be limited. It is not the intent of the test program to make an all-encompassing evaluation of VOST sampling and analysis procedures or to develop new methods. The variety of organic compounds to which the method will inevitably be applied, the almost unlimited number of permutations that could be conceived for experimentation, and time and budget constraints make a comprehensive evaluation (or development of a new methodology) impractical, if not impossible. Nevertheless, keeping an open mind and recording the observations made during all phases of the validation program are important so that the secondary objectives (recommendations relative to method changes, improvements, equipment specifications, quality assurance measures, or other aspects of VOST sampling and analysis) can be accomplished.

If a second field testing program is considered, it should include an assessment of sample stability. Under the essentially ideal laboratory conditions of Phase I, sample holding time (the time between collection and analysis) had a significant effect on TCFM only. Sample stability must be evaluated when the samples are exposed to the constituents present in an incinerator gas stream (e.g., nitrogen oxides, moisture, and hydrogen chloride) to determine whether the 2-week holding time limit in the protocol is appropriate. This limitation may be too restrictive for some compounds and therefore place an unnecessary constraint on testing firms. In some instances, holding the samples for up to 2 weeks may cause a significant decrease in recoveries, as was the case for TCFM in the laboratory study. Sample stability tests should be conducted at a minimum target compound level of approximately 200 ng.

For several reasons, a second field testing program should also include a series of tests to determine if the sample volume affects observed concentrations. For example, the protocol allows the collection of 5 and 20 liters of gas sample at three different flow rates, and the Phase I results were not conclusive regarding the effect of sample volume on observed concentrations. Also, although some of the ruggedness test data suggested that sample volume did have an effect on recoveries, the observed effect may have been due to an increase in errors when the amounts of target compounds in the sample were less than approximately 20 ng. In addition, as pointed out in a technical paper by J. F. Walling,* simultaneous collection of different sample volumes permits determination of the presence of unknown complicating factors (e.g., quantitative retention, blank corrections, and artifact formation). The potential for artifact formation should be greater in an incinerator stack gas than in ambient air.

For evaluation of the effects of using the different sample volumes allowed in the protocol, a distributed air volume test series should be considered in which 5 and 20 liters of sample gas are collected. These volumes correspond to sampling rates of 0.25 and 1 liter per minute over the same 20-minute period. The stack gas matrix should be spiked to ensure that approximately 200 ng of each target compound is added to the 5-liter samples.

The following items were initially considered for evaluation, but are also outside the scope of the current validation project.

- Repetition of the recommended precision, accuracy, and sampling stability tests at a second incinerator site.

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*Walling, J. F. The Utility of Distributed Air Volume Sets When Sampling Ambient Air Using Solid Adsorbents. Atmospheric Environment, 18(4):855-859, 1984.

- If the revised protocol includes the use of the ST trap design, conductance of field tests to determine their precision, accuracy, and sample stability.

- Determination of precision, accuracy, and sample stability for the ND train design at a second level, lower than the one recommended for the Phase II field test.

- Establishment of the reusability of Tenax sorbent after exposure to incinerator stack gas matrices. Reconditioned Tenax will be used because the protocol allows it and because Tenax is expensive. Simply establishing the cleanliness of reused Tenax may not detect changes in sorptive characteristics.

- The use of more Tenax in the front trap and a single sorbent in the backup trap to allow sample desorption conditions to be set as appropriate for the different sorbents.

- Investigation of the use of other sorbents, such as carbon molecular sieve to replace the charcoal, or Tenax TA to replace Tenax GC.

- Consideration of including in the protocol alternative calibration procedures such as the use of gas bottle standards or permeation devices instead of methanolic standards. These have been studied for other Tenax applications and found acceptable.

- Establishment of a step-by-step procedure to validate the protocol for other compounds as the need arises.

- Development and validation of procedures for desorbing multiple samples onto a single pair of traps for analysis or deletion from the protocol of the option for multiple desorption.

- Development and specification of criteria regarding the necessity of recovering and analyzing any aqueous condensate. The recovery procedure specified in the protocol should be revised to be more consistent with the amount of condensate typically collected.

APPENDIX A

STATISTICAL ANALYSIS PROCEDURE

APPENDIX A

ANOVA MODEL

The data for each concentration of the prepared gas stream were analyzed by a two-way ANOVA based upon the model:

$$Y_{ijk} = \mu + Q_i + T_j + QT_{ij} + A_{k(ij)}$$

where

Y_{ijk} = measured concentration of the target compound

μ = constant (overall mean)

Q_i = effect of quad, i = 1,2,3, random

T_j = effect of sampling train (ND or ST), j = 1,2, fixed

QT_{ij} = interaction between sampling trains and quad

$A_{k(ij)}$ = effect of replicate measurements for the j^{th} sampling train in the i^{th} quad

The analysis of variance table for this model is shown in Table A-1. The required computations for the ANOVA were performed by a computer using the Statistical Package for the Social Sciences (SPSS), Version 8.0, September 1, 1980.

TABLE A-1. ANALYSIS OF VARIANCE

Source of variation	Degrees of freedom	Sum of square	Mean square	Average value of mean square
Between quads	2	S_i	$S_i/2$	$\sigma^2 + 4\sigma_Q^2$
Between trains	1	S_j	$S_j/1$	$\sigma^2 + 2\sigma_{QT}^2 + 6\sigma_T^2$
Interaction (quad vs. train)	2	S_{ij}	$S_{ij}/2$	$\sigma^2 + 2\sigma_{QT}^2$
Between replicates	6	$S_{k(ij)}$	$S_{k(ij)}/6$	σ^2
Total	11	S		

$$S_i = 4\, \Sigma_i\, (\bar{x}_{i.} - \bar{x})^2$$

$$S_j = 6\, \Sigma_j\, (\bar{x}_{.j} - \bar{x})^2$$

$$S_{ij} = 2\, \Sigma_{ij}\, (\bar{x}_{ij} - \bar{x}_{i.} - \bar{x}_{.j} + \bar{x})^2$$

$$S_{k(ij)} = \Sigma_{ijk}\, (x_{ijk} - \bar{x}_{ij})^2$$

$$S = \Sigma_{ijk}\, (x_{ijk} - \bar{x})^2$$

EXAMPLE APPLICATION OF ANOVA

Applications of SPSS ANOVA is illustrated below using the results of benzene analyses of dry test gas at 15 ppb shown in Table A-2. As can be seen from Table A-2, the average benzene concentration over the three quads was 57.03 ng/liter for the neck-down sampling train and 53.01 ng/liter for the suspended-tube sampling train.

TABLE A-2. SUMMARY OF BENZENE ANALYSES FOR DRY TEST GAS AT 15 ppb

Quad	Sampling train		Grand average
	Neck-down	Suspended-tube	
1	49.54 50.58	53.35 54.24	
Average	50.06	53.80	51.93
2	87.15 50.12	55.89 51.15	
Average	68.64	53.52	61.08
3	51.89 52.91	50.50 52.92	
Average	52.40	51.71	52.06
Grand average	57.03	53.01	55.02

Table A-3 presents the results of the SPSS ANOVA.

TABLE A-3. ANALYSIS OF VARIANCE OF BENZENE FOR DRY TEST GAS AT 15 ppb

Source of variation	Sum of squares	Degrees of freedom	Mean square
Between quads	220.192	2	110.96
Between trains	48.562	1	48.562
Interaction (quad vs. train)	194.328	2	97.164
Between replicates	701.230	6	116.872
Total	1164.311	11	

The significance testing of the results presented in Table A-3 is described below.

(1) $\sigma^2_{QT} = 0$ This hypothesis is listed by forming the variance ratio

$$F = \frac{97.164}{116.872} = 0.831$$

Since the computed value F = 0.831 is less than the significant value $F_{2,6,0.10} = 3.463$ it is concluded that $\sigma^2_{QT} = 0$ and that there is no statistically significant interaction between the quad and the sampling train.

(2) $\sigma^2_T = 0$ Because the interaction was not significant, the sum of squares for interaction can be pooled with the sum of squares for between replicate with 8 degrees of freedom is

$$\frac{194.328 + 701.230}{2 + 6} = 111.94$$

The variance ratio to test this hypothesis is

$$F = \frac{48.562}{111.94} = 0.434$$

Since the computed value, F = 0.434, is less than the significant value $F_{1,8,0.10} = 3.458$, it is concluded that $\sigma^2_T = 0$ and that there is no difference between the concentration of benzene as determined by the two sampling trains.

(3) $\sigma_Q^2 = 0$ This hypothesis is tested by the variance ratio;

$$F = \frac{110.096}{116.872} = 0.95$$

Since the computed value F = 0.95 is less than the significant value, $F_{2,6,0.10} = 3.143$, it is concluded that $\sigma_Q^2 = 0$ and that there is no difference between the concentration of benzene as determined by the three separate quad test runs.

CALCULATION OF ESTIMATED VALUES

The method used to calculate estimated values is that described by Bennett and Franklin.[a] This technique inserts estimated values which will cause the residual variance to be a minimum. Having inserted the estimated value, the ANOVA was made; however, it was necessary to reduce the number of degrees of freedom by the number of values which were inserted.

To illustrate the application of this procedure, consider the results for vinyl chloride as shown in Table A-4.

TABLE A-4. TEST RESULTS FOR VINYL CHLORIDE AT 15 ppb FOR THE PREPARED GAS
(concentration in ng/liters)

Quad	Neck down	Suspended tube
1	30.82 35.51	6.57 4.84
2	45.69 1.75	5.21 4.26
3	35.11 38.48	2.83 7.80

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[a] Bennett, C. A. and N. L. Franklin. "Statistical Analysis in Chemistry and the Chemical Industry." John Wiley and Sons, New York. 1954. pp. 379-385.

For this situation, the letter "a" will be used to replace the value 1.75. The usual calculations required in a two-way ANOVA (without interaction) is followed. The so-called sums of squares of deviation about the means are calculated for sources of variation including between sampling trains, between quads, and between observations as shown below in Table A-5.

TABLE A-5. CALCULATION OF SUMS OF SQUARES

Quad	Neck down	Suspended tube	Totals
1	30.82	6.57	
	35.51	4.84	77.74
2	45.69	5.21	
	a	4.26	55.16 + a
3	35.11	2.83	
	38.48	7.80	84.22
Total	185.61 + a	31.51	217.12 + a

(a) Correction term: $C = \frac{1}{12}(217.12 + a)^2$

(b) Between trains $= \frac{1}{6}[(185.61 + a)^2 + (31.51)^2] - C$

(c) Between quads $= \frac{1}{4}[(77.74)^2 + (55.16 + a)^2 + (84.22)^2] - C$

(d) Between observations $= [(30.82)^2 + (35.51)^2 + \ldots + a^2 + \ldots + (7.80)^2] - C$

$$Q = (d) - (b) - (c)$$

$$= [(30.82)^2 + (35.5)^2 + \ldots + a^2 + \ldots + (7.80)^2] + \frac{1}{12}(217.12 + a)^2$$

$$- \frac{1}{6}[(185.61 + a)^2 + (31.51)^2] - \frac{1}{4}[(77.74)^2 + (56.16 + a)^2 + (84.22)^2]$$

Combining terms and deleting all purely numerical terms yields:

$$Q = \frac{2\,a^2}{3} - 53.2624\,a$$

Find the value for "a" by taking the partial derivative of Q with respect to "a" and setting the result equal to zero.

$$\frac{\partial Q}{\partial a} = \frac{4a}{3} - 53.2624 = 0$$

$$a = 39.95$$

The value $a = 39.95$ was then inserted in place of 1.75 and the ANOVA was performed and the degrees of freedom was reduced by one.

BARTLETT'S TEST FOR HOMOGENEITY OF VARIANCE

The VOST sampling yields duplicate analyses for each of the two types of sampling trains. A sampling variance (S^2) can be computed for each set of duplicate analyses. If there are (a) estimates S_i^2, each with the same number of degrees of freedom (f), the Bartlett test criterion is

$$M = [\Sigma f_i \ln \bar{S}^2 - \Sigma f_i \ln S_i^2]$$

where $\bar{S}^2 = \frac{\Sigma S_i^2}{a}$

On the null hypothesis that each sampling variance (S_i^2) is an estimate of the same population variance (σ^2), the quantity M/C is distributed approximately as chi-square (X^2) with (a-1) degrees of freedom, where

$$C = 1 + \frac{a + 1}{3a\ f} =$$

Application of Bartlett's Test is illustrated using the set of five sampling variances (S_i^2), calculated for vinyl chloride analyses from Quads 1, 2, and 3 (Table A-6). Five rather than six sampling variances are used because one data value in one of the duplicate analyses was known to be grossly in error. For this example the sampling variance ranged from 0.4489 to 12.3201. The value of X^2 was calculated to be 2.05. Referring to a table of the chi-square distribution, it is determined that for ($a - 1 = 4$) degrees of freedom and a probability of 0.05 the significant value of $X^2_{4,0.05}$ is equal to 11.07. Because the calculated value of $X^2 = 2.05$ is less than the significant value, there is not sufficient cause to reject the hypothesis of common variance.

TABLE A-6. APPLICATION OF BARTLETT'S TEST FOR HOMOGENEITY OF VARIANCE

Train	S	S^2	$\ln S^2$
ND	3.32	11.0224	2.3999
ND	[a]		
ND	2.38	5.6644	1.7342
ST	1.22	1.4884	0.3977
ST	0.67	0.4489	-0.8010
ST	3.51	12.3201	2.5112
		30.9442	6.2420

[a] The sampling standard deviation for this pair of data could not be calculated due to one spurious value.

$$\bar{S}^2 = \frac{\Sigma S^2}{5} = \frac{30.9442}{5} = 6.1888$$

$$M = [5 \ln \bar{S}^2 - \Sigma \ln S^2]$$

$$= [5 \ln 6.1888 - 6.2420]$$

$$= 2.87$$

$$C = 1 + \frac{a + 1}{3a\ f} = 1 + \frac{5 + 1}{(3)(5)(1)} = 1.4$$

$$X^2 = \frac{M}{C} = \frac{2.87}{1.4} = 2.05$$

$$X^2_4,\ 0.05 = 11.07$$

ANOVA calculations for the comparisons between trains are presented in Tables A-7 through A-18. Calculations for the wet runs using the t-statistic are presented in Tables A-19 and A-20. If the difference between trains was significant, the best probability level is shown. For example, all data were tested for significance at the 10 percent probability level. If the probability level calculated by the statistical test was 1 percent, then the 1 percent value was reported. ANOVA calculations for the effect of sample holding time are presented in Table A-21 through A-26.

TABLE A-7. ANOVA - VINYL CHLORIDE 0.5 ppb (DRY)

Source of variation	Sum of squares	Degrees of freedom	Mean square
Between quads	0.055	2	0.0275
Between trains	0.533	1	0.5330
Interaction	0.003	2	0.0015
Between replicates	0.034	5	0.0068
Total	0.624	10[a]	

(1) Interaction $\sigma^2_{QT} = 0 : F = \frac{0.0015}{0.0068} = 0.22$ Not Significant[b]

(2) Pool sum of squares and degrees of freedom for interaction and between replicates

$$\frac{0.034 + 0.003}{5 + 2} = 0.0053$$

$\sigma^2_T = 0 : F = \frac{0.5330}{0.0053} = 100.57$ Significant $\rho < 0.01$[c]

(3) $\sigma^2_Q = 0 : F = \frac{0.0275}{0.0068} = 4.04$ Significant $\rho < 0.10$[b]

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[a] One degree of freedom was lost due to estimation of value to replace incorrect value.

[b] $F_{2,5,0.10} = 3.78$.

[c] $F_{1,7,0.01} = 12.25$.

TABLE A-8. ANOVA - VINYL CHLORIDE 15 ppb (DRY)

Source of variation	Sum of squares	Degrees of freedom	Mean square
Between quads	38.525	2	19.262
Between trains	3137.950	1	3137.950
Interaction	57.559	2	28.780
Between replicates	47.448	5	9.490
Total	3281.483	10[a]	

(1) Interaction $\sigma^2_{QT} = 0 : F = \frac{28.780}{9.490} = 3.03$ Not Significant[b]

(2) Pool sum of squares and degrees of freedom for interaction and between replicates

$$\frac{47.448 + 57.559}{5 + 2} = 15.001$$

$\sigma^2_T = 0 : F = \frac{3137.950}{15.001} = 209$ Significant $\rho < 0.01$[c]

(3) $\sigma^2_Q = 0 : F = \frac{19.262}{9.490} = 2.03$ Not Significant[b]

[a] One degree of freedom was lost due to estimation of value to replace incorrect value.

[b] $F_{2,5,0.10} = 3.78$.

[c] $F_{1,7,0.01} = 12.25$.

TABLE A-9. ANOVA - TRICHLOROFLUOROMETHANE 0.5 ppb (DRY)

Source of variation	Sum of squares	Degrees of freedom	Mean square
Between quads	5.360	2	2.680
Between trains	0.014	1	0.014
Interaction	0.493	2	0.247
Between replicates	4.448	5	0.890
Total	10.315	10[a]	

(1) $\sigma^2_{QT} = 0 : F = \frac{0.247}{0.890} = 0.28$ Not Significant[b]

(2) Pool sum of squares and degrees of freedom for interaction and between replicates

$$\frac{4.448 + 0.493}{5 + 2} = 0.706$$

$\sigma^2_{T} = 0 : F = \frac{0.014}{0.706} = 0.02$ Not Significant[c]

(3) $\sigma^2_{Q} = 0 : F = \frac{2.680}{0.890} = 3.01$ Not Significant[b]

[a] One degree of freedom was lost due to estimation of value to replace incorrect value.

[b] $F_{2,5,0.10} = 3.78$.

[c] $F_{1,7,0.10} = 3.59$.

TABLE A-10. ANOVA - TRICHLOROFLUOROMETHANE 15 ppb (DRY)

Source of variation	Sum of squares	Degrees of freedom	Mean square
Between quads	827.217	2	413.609
Between trains	678.304	1	678.304
Interaction	232.822	2	116.411
Between replicates	283.222	5	56.644
Total	2021.566	10[a]	

(1) $\sigma^2_{QT} = 0 : F = \frac{116.411}{56.644} = 2.06$ Not Significant[b]

(2) Pool sum of squares and degrees of freedom for interaction and between replicates

$$\frac{283.222 + 232.822}{5 + 2} = 73.721$$

$\sigma^2_{T} = 0 : F = \frac{678.304}{73.721} = 9.20$ Significant $\rho < 0.05$[c]

(3) $\sigma^2_{Q} = 0 : F = \frac{413.609}{56.644} = 7.30$ Significant $\rho < 0.05$[d]

[a] One degree of freedom was lost due to estimation of value to replace incorrect value.

[b] $F_{2,5,0.10} = 3.78$.

[c] $F_{1,7,0.05} = 5.59$.

[d] $F_{2,5,0.05} = 5.79$.

TABLE A-11. ANOVA - CHLOROFORM 0.5 ppb (DRY)

Source of variation	Sum of squares	Degrees of freedom	Mean square
Between quads	0.110	2	0.055
Between trains	0.006	1	0.006
Interaction	0.009	2	0.005
Between replicates	0.046	5	0.009
Total	0.171	10[a]	

(1) $\sigma^2_{QT} = 0 : F = \frac{0.005}{0.009} = 0.56$ Not Significant[b]

(2) Pool sum of squares and degrees of freedom for interaction and between replicates

$$\frac{0.046 + 0.009}{5 + 2} = 0.008$$

$\sigma^2_{T} = 0 : F = \frac{0.006}{0.008} = 0.75$ Not Significant[c]

(3) $\sigma^2_{Q} = 0 : F = \frac{0.055}{0.009} = 6.11$ Significant $\rho < 0.05$[d]

[a] One degree of freedom was lost due to estimation of value to replace incorrect value.

[b] $F_{2,5,0.10} = 3.78$.

[c] $F_{1,7,0.10} = 3.59$.

[d] $F_{2,5,0.05} = 5.79$.

TABLE A-12. ANOVA - CHLOROFORM 15 ppb (DRY)

Source of variation	Sum of squares	Degrees of freedom	Mean square
Between quads	477.197	2	238.598
Between trains	134.737	1	134.737
Interaction	153.377	2	76.688
Between replicates	1061.319	6	176.886
Total	1826.629	11	

(1) $\sigma_{QT}^2 = 0 : F = \frac{76.688}{176.886} = 0.43$ Not Significant[a]

(2) Pool sum of squares and degrees of freedom for interaction and between replicates

$$\frac{1061.319 + 153.377}{6 + 2} = 151.837$$

$\sigma_T^2 = 0 : F = \frac{134.737}{151.837} = 0.89$ Not Significant[b]

(3) $\sigma_Q^2 = 0 : F = \frac{238.598}{176.886} = 1.35$ Not Significant[a]

[a] $F_{2,6,0.10} = 3.46$.

[b] $F_{1.8,0.10} = 3.46$.

TABLE A-13. ANOVA - CARBON TETRACHLORIDE 0.5 ppb (DRY)

Source of variation	Sum of squares	Degrees of freedom	Mean square
Between quads	0.535	2	0.268
Between trains	0.635	1	0.635
Interaction	0.024	2	0.012
Between replicates	0.202	5	0.040
Total	1.396	10[a]	

(1) $\sigma^2_{QT} = 0 : F = \frac{0.012}{0.040} = 0.30$ Not Significant[b]

(2) Pool sum of squares and degrees of freedom for interaction and between replicates

$$\frac{0.202 + 0.024}{5 + 2} = 0.032$$

$\sigma^2_{T} = 0 : F = \frac{0.635}{0.032} = 19.84$ Significant $\rho < 0.01$[c]

(3) $\sigma^2_{Q} = 0 : F = \frac{0.268}{0.040} = 6.70$ Significant $\rho < 0.05$[d]

[a] One degree of freedom was lost due to estimation of value to replace incorrect value.

[b] $F_{2,5,0.10} = 3.78$.

[c] $F_{1,7,0.01} = 12.25$.

[d] $F_{2,5,0.05} = 5.79$.

TABLE A-14. ANOVA - CARBON TETRACHLORIDE 15 ppb (DRY)

Source of variation	Sum of squares	Degrees of freedom	Mean square
Between quads	323.308	2	161.654
Between trains	482.094	1	482.094
Interaction	39.919	2	19.960
Between replicates	1850.370	6	308.395
Total	2695.691	11	

(1) $\sigma^2_{QT} = 0 : F = \frac{19.960}{308.395} = 0.06$ Not Significant[a]

(2) Pool sum of squares and degrees of freedom for interaction and between replicates

$$\frac{1850.370 + 39.919}{6 + 2} = 236.286$$

$\sigma^2_{T} = 0 : F = \frac{482.094}{236.286} = 2.04$ Not Significant[b]

(3) $\sigma^2_{Q} = 0 : F = \frac{161.654}{308.395} = 0.52$ Not Significant[a]

[a] $F_{2,6,0.10} = 3.46$.

[b] $F_{1,8,0.10} = 3.46$.

TABLE A-15. ANOVA - BENZENE 0.5 ppb (DRY)

Source of variation	Sum of squares	Degrees of freedom	Mean square
Between quads	2.969	2	1.484
Between trains	0.187	1	0.187
Interaction	0.137	2	0.070
Between replicates	5.868	5	1.174
Total	9.161	10[a]	

(1) $\sigma^2_{QT} = 0 : F = \frac{0.070}{1.174} = 0.06$ Not Significant[b]

(2) Pool sum of squares and degrees of freedom for interaction and between replicates

$$\frac{5.868 + 0.137}{5 + 2} = 0.858$$

$\sigma^2_{T} = 0 : F = \frac{0.187}{0.858} = 0.22$ Not Significant[c]

(3) $\sigma^2_{Q} = 0 : F = \frac{1.484}{1.174} = 1.264$ Not Significant[b]

[a] One degree of freedom was lost due to estimation of value to replace incorrect value.

[b] $F_{2,5,0.10} = 3.78$.

[c] $F_{1,7,0.10} = 3.59$.

TABLE A-16. ANOVA - BENZENE 15 ppb (DRY)

Source of variation	Sum of squares	Degrees of freedom	Mean square
Between quads	220.192	2	110.096
Between trains	48.562	1	48.562
Interaction	194.328	2	97.164
Between replicates	701.230	6	116.872
Total	1164.311	11	

(1) $\sigma^2_{QT} = 0 : F = \frac{97.164}{116.872} = 0.83$ Not Significant[a]

(2) Pool sum of squares and degrees of freedom for interaction and between replicates

$$\frac{701.230 + 194.328}{6 + 2} = 111.944$$

$\sigma^2_{T} = 0 : F = \frac{48.562}{111.944} = 0.43$ Not Significant[b]

(3) $\sigma^2_{Q} = 0 : F = \frac{110.096}{116.872} = 0.94$ Not Significant[a]

[a] $F_{2,6,0.10} = 3.46$.

[b] $F_{1,8,0.10} = 3.46$.

TABLE A-17. ANOVA - TETRACHLOROETHYLENE 0.5 ppb (DRY)

Source of variation	Sum of squares	Degrees of freedom	Mean square
Between quads	2.277	2	1.138
Between trains	0.203	1	0.203
Interaction	1.377	2	0.689
Between replicates	6.449	5	1.290
Total	10.305	10[a]	

(1) $\sigma^2_{QT} = 0 : F = \frac{0.689}{1.290} = 0.53$ Not Significant[b]

(2) Pool sum of squares and degrees of freedom for interaction and between replicates

$$\frac{6.449 + 1.377}{5 + 2} = 1.118$$

$\sigma^2_{T} = 0 : F = \frac{0.203}{1.118} = 0.18$ Not Significant[c]

(3) $\sigma^2_{Q} = 0 : F = \frac{1.138}{1.290} = 0.88$ Not Significant[b]

[a] One degree of freedom was lost due to estimation of value to replace incorrect value.

[b] $F_{2,5,0.10} = 3.78$.

[c] $F_{1,7,0.10} = 3.59$.

TABLE A-18. ANOVA - TETRACHLOROETHYLENE 15 ppb (DRY)

Source of variation	Sum of squares	Degrees of freedom	Mean square
Between quads	1011.687	2	505.843
Between trains	494.083	1	494.083
Interaction	1204.987	2	602.493
Between replicates	3407.070	6	542.151
Total	6117.827	11	

(1) $\sigma^2_{QT} = 0 : F = \frac{602.493}{542.151} = 1.11$ Not Significant[a]

(2) Pool sum of squares and degrees of freedom for interaction and between replicates

$$\frac{3407.070 + 120.987}{6 + 2} = 576.507$$

$\sigma^2_{T} = 0 : F = \frac{494.083}{576.507} = 0.86$ Not Significant[b]

(3) $\sigma^2_{Q} = 0 : F = \frac{505.843}{542.151} = 0.93$ Not Significant[a]

[a] $F_{2,6,0.10} = 3.46.$

[b] $F_{1,8,0.10} = 3.46.$

APPLICATION OF t-TEST

A series of eight (i.e., W_1-W_8) test runs were made using wet gas--four each for 0.5 and 15 ppb. Only two of the four sampling trains could be used for these test runs. Each test run was made using either the ND or the ST trains. These results were analyzed using the Student's "t" test, to determine the statistical significance of the difference between the average pollutant concentrations for the ND and ST sampling trains. Results of the comparison of sampling trains for the wet test gas are presented in Tables A-19 and A-20 for 0.5 and 15 ppb gases, respectively.

Application of the Student's "t" test to determine the statistical significance of differences between averages for two independent samples assumes common variance for the two samples; i.e., $(S^2_{ND} = S^2_{ST})$. Before applying the "t" test the assumption of common variance can be tested using the F-ratio test.*

$$F = \frac{\text{Variance (larger)}}{\text{Variance (smaller)}}$$

If the calculated value of F is smaller than $F_{3,3,0.10} = 5.39$, the assumption of common variance is not rejected. The next step is to calculate

$$t = [2(\bar{x}_{ND} - \bar{x}_{ST})]/[s^2_{ND} + s^2_{ST}]^{\frac{1}{2}}$$

where $\bar{x}_{ND}$ = average of four samples using ND train

$\bar{x}_{ST}$ = average of four samples using ST train

s^2_{ND} = variance of the ND train data

s^2_{ST} = variance of the ST train data

If the calculated value of "t" exceeds the value of "t" in the table of the distribution of "t" for six degrees of freedom at a given probability level (i.e., 0.10, 0.05, or 0.01) it is concluded that the two means differ significantly.**

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*"Statistical Methods", George W. Snedecor and William G. Cochran. The Iowa State University Press, Sixth Edition 1967, pp. 116-118

**Ibid, p. 549.

In the siutation where the calculated value of F exceeds $F_{3,3,0.10} = 5.39$, the assumption of common variance is rejected. For this case the calculated value of "t" does not follow the Student's "t" distribution. A procedure known as the Behrens-Fisher test* was used to calculate an adjusted degrees of freedom (d.f.) where,

$$\frac{1}{d.f.} = \frac{1}{3}\left[\left(\frac{S_{ND}^2}{S_{ND}^2 + S_{ST}^2}\right)^2 + \left(\frac{S_{ST}^2}{S_{ND}^2 + S_{ST}^2}\right)^2\right]$$

The adjusted degrees of freedom was rounded off to an integer and used with the table of the Student "t" distribution as previously described.

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*"Statistical Analysis in Chemistry and the Chemical Industry", Carl A. Bennett and Norman L. Franklin. John Wiley 1975, p. 177

TABLE A-19. COMPARISON OF SAMPLING TRAINS, 0.5 ppb WET

Parameter	Average ($\bar{x}$)		Variance (S^2)		F[a] ratio	Common[b] variance	Student[c] t	Probability of[d] difference between averages
	ND	ST	ND	ST				
Vinyl chloride	0.53	0.36	0.0151	0.0060	2.52	Yes	2.268	$\rho < 0.10$, significant
Trichlorofluoromethane	2.74	2.53	0.3365	1.0768	3.20	Yes	0.349	$\rho > 0.10$, not significant
Chloroform	2.02	1.84	0.1852	0.2211	1.43	Yes	0.144	$\rho > 0.10$, not significant
Carbon tetrachloride	2.71	1.63	0.3403	0.2999	1.29	Yes	4.761	$\rho < 0.01$, significant
Benzene	2.48	2.01	0.3743	0.0889	4.21	Yes	1.381	$\rho > 0.10$, not significant
Tetrachloroethylene	3.79	3.55	0.1051	0.0489	2.15	Yes	1.172	$\rho > 0.10$, not significant

[a] $F = \frac{\text{Variance (larger)}}{\text{Variance (smaller)}}$.

[b] Assume common variance if $F < F^{3}_{3,0.10} = 5.39$.

[c] $t = [2(\bar{x}_{ST} - \bar{x}_{ND})]/[S^2_{ST} + S^2_{ND}]^{\frac{1}{2}}$.

[d] IF $t > t_{6,0.10} = 1.943$; then probability <0.10.

IF $t > t_{6,0.05} = 2.447$; then probability <0.05.

IF $t > t_{6,0.01} = 3.707$; then probability <0.01.

TABLE A-20. COMPARISON OF SAMPLING TRAINS, 15 ppb WET

Parameter	Average ($\bar{x}$)		Variance (S^2)		F[a] ratio	Common[b] variance	Student[c] "t"	Probability[d] of difference between averages
	ND	ST	ND	ST				
Vinyl chloride	20.31	19.97	3.1113	13.5660	4.36	Yes	0.166	>0.10, not significant
Trichlorofluoromethane	64.47	33.84	16.2038	32.0628	1.98	Yes	8.817	<0.01, significant
Chloroform	73.34	65.31	5.5545	29.2724	5.27	Yes	2.723	<0.05, significant
Carbon tetrachloride	86.46	53.43	9.1809	3.8844	2.36	Yes	18.276	<0.01, significant
Benzene	52.64	49.35	0.8232	9.3117	11.3116	No	2.065[e]	>0.10, not significant
Tetrachloroethylene	143.4	139.2	14.3368	49.6489	3.46	Yes	1.056	>0.10, not significant

[a] $F = \frac{\text{Variance (larger)}}{\text{Variance (smaller)}}$.

[b] Assume common variance if $F < F^{3}_{3,0.10} = 5.39$.

[c] $t = [2(\bar{x}_{ST} - \bar{x}_{ND})]/[S^2_{ST} + S^2_{ND}]^{\frac{1}{2}}$.

[d] IF $t > t_{6,0.10} = 1.943$; then probability <0.10.

IF $t > t_{6,0.05} = 2.447$; then probability <0.05.

IF $t > t_{6,0.01} = 3.707$; then probability <0.01.

[e] IF $t > t_{4,0.10} = 2.132$; then probability <0.10.

The reduction in degrees of freedom from 6 to 4 results from application of Behrens-Fisher test for case when variances are significantly different.

TABLE A-21. ANOVA - VINYL CHLORIDE 15 ppb (HOLDING TIME)

Source of variation	Sum of squares	Degrees of freedom	Mean square
Between holding times	651.428	2	325.714
Between trains	2386.457	1	2386.457
Interaction	832.696	2	416.348
Between replicates	205.211	13	15.786
Total	4075.793	18[a]	

(1) $\sigma^2_{HT,T} = 0 : F = \frac{416.348}{15.786} = 26$ Significant $\rho < 0.01$[b]

(2) $\sigma^2_{T} = 0 : F = \frac{2386.457}{416.348} = 5.73$ Not Significant[c]

(3) $\sigma^2_{HT} = 0 : F = \frac{325.714}{15.786} = 20.63$ Significant $\rho < 0.05$[b]

[a] One degree of freedom was lost due to estimation of value to replace incorrect value.

[b] $F_{2,13,0.01} = 6.70$.

[c] $F_{1,2,0.05} = 8.53$.

TABLE A-22. ANOVA - TRICHLOROFLUOROMETHANE 15 ppb (HOLDING TIME)

Source of variation	Sum of squares	Degrees of freedom	Mean square
Between holding times	1039.873	2	519.936
Between trains	1342.177	1	1342.177
Interaction	21.695	2	10.848
Between replicates	1388.419	13	106.802
Total	3792.164	18[a]	

(1) $\sigma^2_{HT,T} = 0 : F = \frac{10.848}{106.802} = 0.10$ Not Significant[b]

(2) Pool sum of squares and degrees of freedom for interaction and between replicates

$$\frac{1388.419 + 21.695}{13 + 2} = 94.006$$

$\sigma^2_{T} = 0 : F = \frac{1342.177}{94.006} = 14$ Significant $\rho < 0.01$[c]

(3) $\sigma^2_{HT} = 0 : F = \frac{519.936}{106.802} = 4.87$ Significant $\rho < 0.05$[d]

[a] One degree of freedom was lost due to estimation of value to replace incorrect value.

[b] $F_{2,13,0.10} = 2.76$.

[c] $F_{1,15,0.01} = 8.68$.

[d] $F_{2,13,0.05} = 3.41$.

TABLE A-23. ANOVA - CHLOROFORM 15 ppb (HOLDING TIME)

Source of variation	Sum of squares	Degrees of freedom	Mean square
Between holding times	241.736	2	120.868
Between trains	127.412	1	127.412
Interaction	20.842	2	10.421
Between replicates	1840.186	14	131.442
Total	2230.175	19	

(1) $\sigma^2_{HT,T} = 0 : F = \frac{10.421}{131.442} = 0.08$ Not Significant[a]

(2) Pool sum of squares and degrees of freedom for interaction and between replicates

$$\frac{1840.186 + 20.842}{14 + 2} = 116.314$$

$\sigma^2_{T} = 0 : F = \frac{127.412}{116.314} = 1.09$ Not Significant[b]

(3) $\sigma^2_{HT} = 0 : F = \frac{120.868}{131.442} = 0.92$ Not Significant[a]

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[a] $F_{2,14,0.10} = 2.73$.

[b] $F_{1,16,0.10} = 3.05$.

TABLE A-24. ANOVA - CARBON TETRACHLORIDE 15 ppb (HOLDING TIME)

Source of variation	Sum of squares	Degrees of freedom	Mean square
Between holding times	181.292	2	90.646
Between trains	623.063	1	623.063
Interaction	31.468	2	15.734
Between replicates	2273.568	14	162.398
Total	3109.391	19	

(1) $\sigma^2_{HT,T} = 0 : F = \frac{15.734}{162.398} = 0.10$ Not Significant[a]

(2) Pool sum of squares and degrees of freedom for interaction and between replicates

$$\frac{2273.568 + 31.468}{14 + 2} = 144.065$$

$\sigma^2_{T} = 0 : F = \frac{623.063}{144.065} = 4.32$ Significant $\rho < 0.10$[b]

(3) $\sigma^2_{HT} = 0 : F = \frac{90.646}{162.398} = 0.56$ Not Significant[a]

[a] $F_{2,14,0.10} = 2.73$.

[b] $F_{1,16,0.10} = 3.05$.

TABLE A-25. ANOVA - BENZENE 15 ppb (HOLDING TIME)

Source of variation	Sum of squares	Degrees of freedom	Mean square
Between holding times	101.072	2	50.536
Between trains	63.190	1	63.190
Interaction	19.998	2	6.499
Between replicates	1136.422	14	81.173
Total	1313.682	19	

(1) $\sigma^2_{HT,T} = 0 : F = \frac{6.499}{81.173} = 0.08$ Not Significant[a]

(2) Pool sum of squares and degrees of freedom for interaction and between replicates

$$\frac{1136.422 + 12.998}{14 + 2} = 71.838$$

$\sigma^2_{T} = 0 : F = \frac{63.190}{71.838} = 0.88$ Not Significant[b]

(3) $\sigma^2_{HT} = 0 : F = \frac{50.536}{81.173} = 0.62$ Not Significant[a]

[a] $F_{2,14,0.10} = 2.73$.

[b] $F_{1,16,0.10} = 3.05$.

TABLE A-26. ANOVA - TETRACHLOROETHYLENE 15 ppb (HOLDING TIME)

Source of variation	Sum of squares	Degrees of freedom	Mean square
Between holding times	773.181	2	386.591
Between trains	948.065	1	948.065
Interaction	9.831	2	4.916
Between replicates	6274.188	14	448.156
Total	8005.266	19	

(1) $\sigma^2_{HT,T} = 0 : F = \frac{4.916}{448.156} = 0.01$ Not Significant[a]

(2) Pool sum of squares and degrees of freedom for interaction and between replicates

$$\frac{6274.188 + 9.831}{14 + 2} = 392.751$$

$\sigma^2_{T} = 0 : F = \frac{948.065}{392.751} = 2.41$ Not Significant[b]

(3) $\sigma^2_{HT} = 0 : F = \frac{386.591}{448.156} = 0.86$ Not Significant[a]

[a] $F_{2,14,0.10} = 2.73$.

[b] $F_{1,16,0.10} = 3.05$.

APPENDIX B

SORBENT TRAP PREPARATION, CONDITIONING, AND PRETEST BLANK CHECKING

SORBENT TRAP PREPARATION, CONDITIONING, AND PRETEST BLANK CHECKING

This appendix describes the preparation of the reagent and materials, the assembly and conditioning of the sorbent traps, and pretest blank checking of conditioned traps. Because various combinations of trap-conditioning measures were tried over the course of the laboratory study, recommendations regarding the procedures are also addressed. Also included at the end of the appendix is the comparison between charcoal extracted with methanol and unextracted charcoal.

REAGENT AND MATERIALS PREPARATION

Tenax, 35/60 Mesh (2,6-Diphenylene Oxide Polymer)

A single lot of Tenax was used throughout the laboratory study. Raw Tenax as received from the supplier was Soxhlet-extracted for 24 hours with glass-distilled methanol (Burdick and Jackson pesticide residue grade or equivalent). The Tenax was transferred to a clean ceramic evaporating dish and dried for 4 hours under an infrared lamp in an exhaust hood. This step was added to avoid sudden, violent boiling of methanol in the vacuum oven which can splatter the Tenax granules. The evaporating dish filled with partially dried Tenax was then placed in a vacuum oven at 50°C and 20 in.Hg vacuum for 6 hours to complete the drying. In the VOST preparation room, the Tenax was then transferred to a clean, amber glass bottle with a Teflon-lined screw cap and placed in a sealed glass aquarium containing activated charcoal for storage until it was packed into sorbent traps.

The general quality of the Tenax batch was checked by analyzing several preliminary Tenax traps at the beginning of the study and assessed by two independent laboratories. Three traps from the first conditioning batch of the inner ST Tenax traps were analyzed by GC/MS as regular samples. Immediately prior to the analysis of these traps, proper operation of the GC/MS system was verified by analyzing three different recovery check standards and conducting a system blank check. The three Tenax trap samples were very similar to the system blank except for the presence of several heavily used laboratory solvents (e.g., acetone, methylene chloride, and hexane). The traps contained less than 2 ng of benzene or tetrachloroethylene, and none of the other four target compounds was detected.

One 15-g bottle of the raw Tenax (as received from the supplier) was supplied to each of two independent laboratories for assessment of general Tenax quality. Each laboratory processed the Tenax differently, following its own procedures, and analyzed at least six traps. Both laboratories reported that the Tenax was of typical quality. One laboratory indicated that the benzene content was approximately 20 ng per trap, whereas the other one reported approximately 2 or less ng per similar size trap.

Charcoal

A single lot of Calgon-Type GW20X50, petroleum-based charcoal was used throughout the study. New charcoal was extracted and dried in the manner just described for Tenax.

The extraction procedures are not recommended for the charcoal, as better blank values have been obtained with unextracted charcoal. Of course, whether extraction is needed may depend on the particular batch of charcoal being used. The recommended procedure is to heat the new charcoal in a vacuum oven at a temperature of 190°C for about 6 hours under a slow nitrogen purge (approximately 50 ml per minute) and moderate vacuum (approximately 125 mmHg).

O-Rings

The Viton O-rings used for ST traps were cleaned ultrasonically for 15 minutes in a hot, nonionic detergent (Alcojet) solution. The rings were then thoroughly rinsed with charcoal-filtered deionized water, air-dried on aluminum foil in the VOST preparation room, and baked in a vacuum oven for 48 hours at 200°C and 20 in. Hg vacuum. The O-rings were then stored in glass bottles with Teflon-lined screw caps and placed in sealed glass aquariums containing activated charcoal where they stayed until used.

Glassware and Teflon Parts

All glass parts (traps, culture tubes, flasks, trap caps, and condensers), Teflon fittings, and sample-exposed connecting lines were cleaned with a nonionic detergent (Alcojet) and rinsed thoroughly with charcoal-filtered deionized water. The cleaned parts were then oven-dried at 110°C for 2 or more hours in the VOST preparation room. All glassware was placed in sealed glass aquariums containing activated charcoal and stored in the VOST preparation room until used. Immediately prior to their need, parts were removed from aquariums and transported to the sampling location in carrying cases. Sampling train glassware and Teflon fittings were wrapped in aluminum foil.

Metal Parts

C-clips, screens, and ND trap end plugs (also stainless steel unions used to connect traps in the sampling train) were cleaned ultrasonically for 15 minutes in a hot, nonionic detergent (Alcojet) solution; rinsed with charcoal-filtered deionized water; air-dried on aluminum foil in the VOST preparation room; and heated in a muffle furnace at 400°C for 2 hours. The cleaned parts were placed separately in bottles with Teflon-lined screw caps and stored in sealed glass aquariums containing activated charcoal until used.

The stainless steel unions used to make sample train connections were prepared initially as described. After a week's tests the unions were recleaned in the manner described for glassware and Teflon fittings prior to reuse. The Supeltex M-1 ferrules were discarded with each recleaning.

Glass Wool

Pyrex wool filtering fiber was Soxhlet-extracted for 16 hours with glass-distilled pentane (Burdick and Jackson, pesticide residue grade or equivalent), placed in a clean ceramic evaporating dish, and dried under an infrared lamp in an exhaust hood for 4 hours. The dish filled with glass wool was then placed in a vacuum oven at 110°C and 20 in.Hg vacuum for 6 hours to complete the drying. Clean glass wool was placed in amber glass bottles with Teflon-lined screw caps and stored in a sealed glass aquarium containing activated charcoal in the VOST preparation room until used.

A preliminary check of the first batch of pentane-extracted glass wool indicated the presence of residual pentane; therefore, the first batch of wool was reextracted and dried as previously described except that the solvent was methanol. Subsequent batches of glass wool were extracted only with methanol.

Charcoal (for Storage Containers)

New activated charcoal was preferred for use in storage containers for reagents and materials (aquariums for cleaned parts and sorbents, and metal cans for assembled traps). All charcoal for such use was prepared by baking at 250°C under 20 in.Hg vacuum for at least 8 hours.

Water

Charcoal-filtered, deionized water was used for leak-checking assembled sorbent traps.

Nitrogen

Nitrogen gas used for purging sorbent traps during thermal conditioning was passed through an inline gas purifier containing 5A° molecular sieve and activated charcoal. The charcoal bed in the gas purifier was replaced with each new nitrogen cylinder.

ASSEMBLY OF VOST SORBENT TRAPS

All of the sorbent traps were assembled and packed in a reverse-flow ventilation hood with a charcoal filter on the air intake. The assembly hood was located in the VOST preparation room. Nylon gloves were worn during the assembly steps to avoid contamination with skin oils.

A modified rifle-shell loader was used to load the sorbents into the glass traps. The apparatus was calibrated at three different settings to deliver either 1.6 grams of Tenax, 1.0 gram of Tenax, or 1.0 gram of charcoal. Tenax traps were loaded with 1.6 grams of Tenax and Tenax/charcoal traps were loaded with 1.0 gram of each sorbent. A small section of Teflon tubing was used to transfer the sorbent from the loader into the ND sorbent traps. No tubing was needed for the ST traps, which had larger openings.

For the ST traps, sorbent beds were held in place by stainless steel screens and zinc-coated steel C-clips; for the ND traps, they were held in place by glass wool plugs inserted with the aid of a GC column packing tool. The sorbent beds in the Tenax/charcoal tubes were separated from each other in the same way. Packed sorbent traps were stored in clean glass-culture tubes with Teflon-lined screw caps to prevent contamination between preparation steps. A small plug of clean glass wool was placed in the bottom of the culture tube to cushion the sorbent trap. At this stage of assembly the ST trap consisted of the inner glass tube packed with sorbent. The ST inner trap was not assembled into the protective outer glass trap with O-rings to form the complete ST trap until after the inner traps were thermally conditioned. All of the packed sorbent traps (inside culture tubes) were kept in sealed glass aquariums containing activated charcoal between preparation steps.

All sorbent traps were labeled with a numeric code by etching the glass to facilitate documentation of the exact handling of each trap during preparation and conditioning. After each trap was packed, the trap packer recorded the trap and culture tube numbers, reagent batch numbers, and storage location in the log book.

CONDITIONING PROCEDURES

Sorbent traps were conditioned by purging with approximately 30 ml/min of nitrogen at elevated temperatures. A schematic of the conditioning apparatus is shown in Figure B-1. Conditioning procedures are described separately for the ST and ND traps. All conditioning batch data were recorded in log books to document the treatment of each trap. Several combinations of conditioning times and temperatures were tried over the course of the laboratory study in efforts to obtain lower and more consistent blank values.

The ST inner traps were conditioned in a Nutech 14-chamber multiple desorber with temperature controller. The nitrogen purge flow was set at approximately 30 ml/min per trap. The purge gas flow was split into four separate supply lines, each controlled individually with line restrictions. Two of the lines supplied gas to separate groups of three chambers; the other two lines supplied gas to two four-chamber groups. Flow measurements were

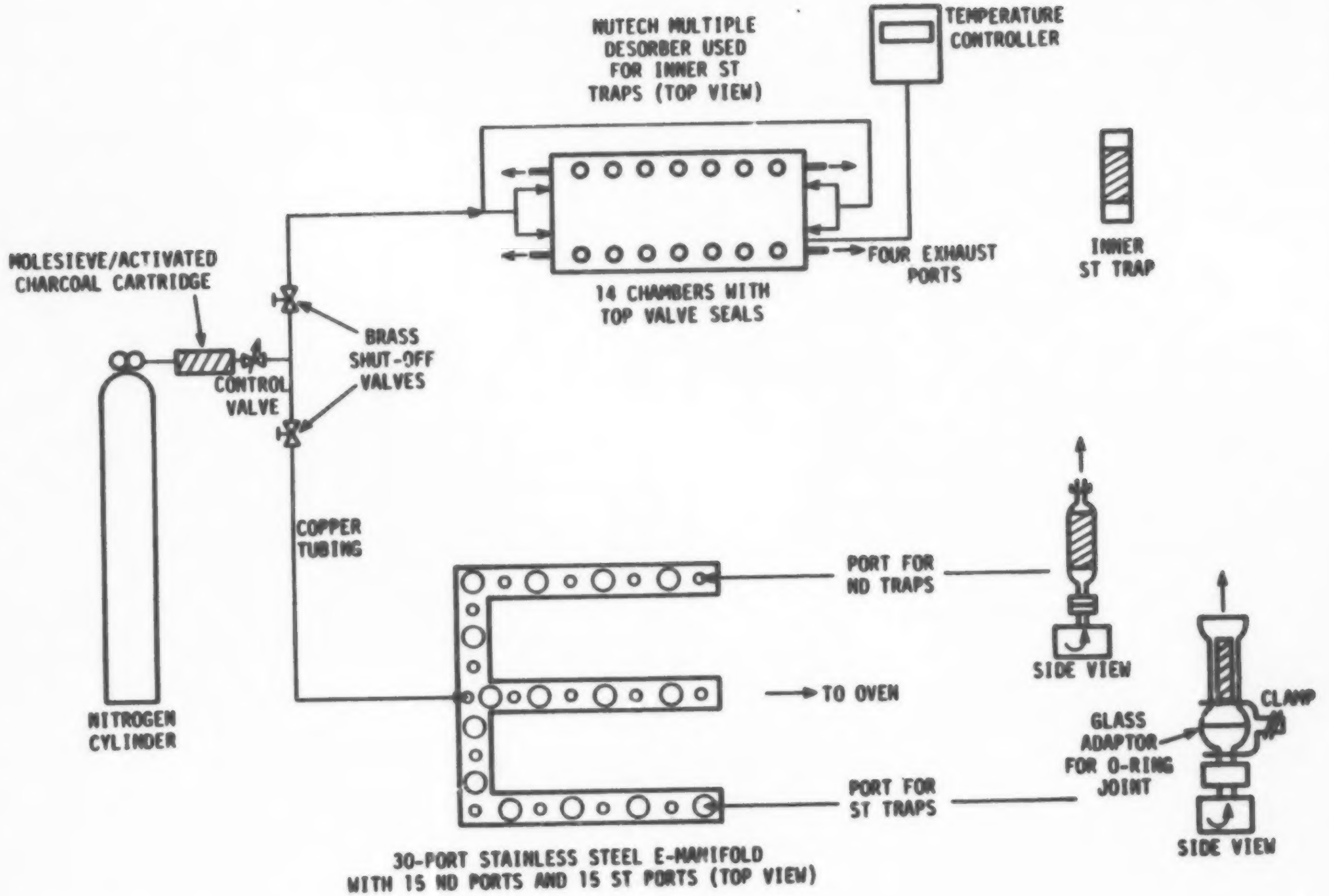

NUTECH MULTIPLE
DESORBER USED
FOR INNER ST
TRAPS (TOP VIEW)
TEMPERATURE
CONTROLLER
MOLESIEVE/ACTIVATED
CHARCOAL CARTRIDGE
FOUR EXHAUST
PORTS
INNER
ST TRAP
14 CHAMBERS WITH
TOP VALVE SEALS
BRASS
SHUT-OFF
VALVES
CONTROL
VALVE
COPPER
TUBING
PORT FOR
ND TRAPS
SIDE VIEW
TO OVEN
NITROGEN
CYLINDER
CLAMP
GLASS
ADAPTOR
FOR O-RING
JOINT
PORT FOR
ST TRAPS
SIDE VIEW
30-PORT STAINLESS STEEL E-MANIFOLD
WITH 15 ND PORTS AND 15 ST PORTS (TOP VIEW)

Figure B-1. Schematic of sorbent trap conditioning equipment.

made on the four exhaust ports with a bubble meter after all traps had been inserted into the multiple desorber. Because the direction of purge gas flow within each chamber was downward, Tenax/charcoal traps were inserted with the charcoal portion at the top; this allowed the purge gas to pass through the charcoal first. For all conditioning batches the temperature of the multiple desorber was set at 250°C. Metal forceps were used to transfer the sorbent traps between the culture tubes and the multiple desorber. At the end of a conditioning period the hot traps were removed from the desorber and replaced in the culture tubes to cool. The sorbent traps were then fully assembled by placing two of the smaller O-rings on the inner trap, pushing it into the protective outer glass trap, and capping both ends. Each outer glass piece was etched with a number, as was the inner sorbent trap. Nylon gloves were worn during this assembly step to avoid contamination with skin oil. The final traps containing the inner sorbent traps were then placed in metal cans containing charcoal and refrigerated until assembly.

For some conditioning batches, the fully assembled ST traps received additional thermal conditioning on the E-manifold, whereas others did not. For manifold conditioning, 15 traps were clamped on the manifold ports. All unused ST and ND ports were capped. Purge flow was checked with a bubble meter and O-ring adapter to ensure that at least 30 ml/min was passing through each trap. The manifold was then placed in a preheated laboratory oven for the designated time period. The temperature of the oven was verified with an independent bi-metal dial thermometer. Initial ST manifold batches were conditioned at an oven temperature of 190°C; however, the temperature was reduced (based on blank check results) to 150°C to minimize potential O-ring contamination. At the end of the conditioning batch, the manifold was removed from the hot oven and set aside. Purge flow was maintained until all traps were cooled to room temperature and the tops were capped. The traps were purged during cooling (purged cool-down) at the end of the final conditioning to prevent any ambient contamination from being sucked onto the traps by the vacuum created during cooling. The use of this procedure did decrease the level of ambient contaminants. As each trap was removed, the other end was capped. Conditioned traps were placed in metal cans containing charcoal and stored in a refrigerator.

Initially, the ST traps were conditioned for a single 8-hour period in the multiple desorber followed by a single 2-hour period on the manifold. Subsequently, other combinations of treatment intervals were tried; these consisted of a single 8-hour period in the multiple desorber followed by multiple heating periods on the manifold, four 2-hour periods in the multiple desorber followed by a single interval on the manifold, multiple intervals on both the desorber and manifold, single intervals in the desorber for 16 and 24 hours (no manifold conditioning), and multiple extended intervals in the desorber (no manifold conditioning). For multiple heating intervals, the trap was allowed to cool to room temperature between periods. An evaluation of the pretest blank-check results (presented later) indicated that no particular combination was clearly superior to any other; however, conditioning on the manifold did not seem to be necessary.

All conditioning of the ND traps was performed on the E-manifold. Fifteen traps per batch were connected to the manifold ND ports with their threaded fittings. All unused ports were capped. Purge flow was set and checked with a bubble meter so that the minimum flow at each trap measured approximately 30 ml/min. All Tenax/charcoal traps conditioned on the manifold (either ND or ST) were positioned so that the purge gas entered the charcoal end first.

The entire manifold was purged approximately 5 minutes to remove air. The manifold was placed in the preheated oven, and the traps were conditioned for the specified time interval at a temperature of 190°C. At the end of the conditioning interval, the manifold was removed from the hot oven and set aside. While still hot, each trap was checked with a bubble meter for positive flow. Purge flow was maintained until all traps were cooled to room temperature and the tops capped. As each trap was removed, the other end was capped. Conditioned traps were replaced in culture tubes, which were placed in friction-top metal cans with a layer of activated charcoal and then refrigerated.

The initial conditioning of ND traps consisted of a single heating period of approximately 16 hours. Other combinations tried during the laboratory validation included multiple 16-hour heating intervals, a 16-hour period followed by one or more 2-hour heating periods, a 24-hour period followed by one or more 2-hour periods, and a single conditioning period of approximately 28 hours. One pair of traps was even conditioned for a single 60-hour period. For any multiple heating intervals the traps were cooled to room temperature between periods. Based on an evaluation of pretest blank data, a single conditioning period of 28 hours or more is recommended. A summary of pretest blank check data for all traps actually used as samples is presented in Section 3.

All ND and ST traps were stored for at least 24 hours between conditioning and blank-checking. The leak-checking step specified in the protocol was performed during the blank-checking process rather than during the conditioning steps.

PRETEST BLANK CHECKING

Tenax and Tenax/charcoal sorbent traps were blank checked after conditioning by use of the apparatus shown in Figure B-2. The trap desorption system consisted of nitrogen carrier gas supplied at approximately 40 ml/min, a forced convection oven operated at 150°C, a heated (250°C) six-port valve to direct nitrogen flows through the system, and a coil of 1/16-in. o.d. stainless steel tubing immersed in liquid nitrogen to trap desorbed organic compounds. The analytical system consisted of a small electric furnace (for rapid heating of the trap to approximately 230°C and flash-vaporizing the trapped components), nitrogen carrier gas, a Perkin Elmer Model 990 GC/FID, and a strip chart recorder. The large convection oven was used so that both ND and ST traps could be blanked on the same system.

Figure B-3 is a schematic of the six-port valve showing the direction of carrier flow for the desorption and analytical systems. As shown, the desorption carrier gas passed through two separate charcoal/molesieve filters before entering the sampling traps to minimize the carrier gas blank value. The GC column and operating conditions were as follows: 1.8 m x 3 mm i.d. SS column packed with 0.2 percent Carbowax 1500 on 60/80 mesh Carbopack C; and a temperature program calling for 70°C for 8 minutes, 24°C/min to 150°C, and holding at 150°C for a total run time of approximately 25 minutes.

The following procedures were used to blank-check and leak-check each pair of sorbent traps.

1) With the six-port valve in the "inject" position, a pair of traps were connected with the charcoal side of the Tenax/charcoal tube connected to the inlet carrier gas line, the traps connected together, and the outlet of the Tenax trap still capped. The ST traps were connected directly to each other with a clamp; the ND traps were connected by means of a stainless steel union.

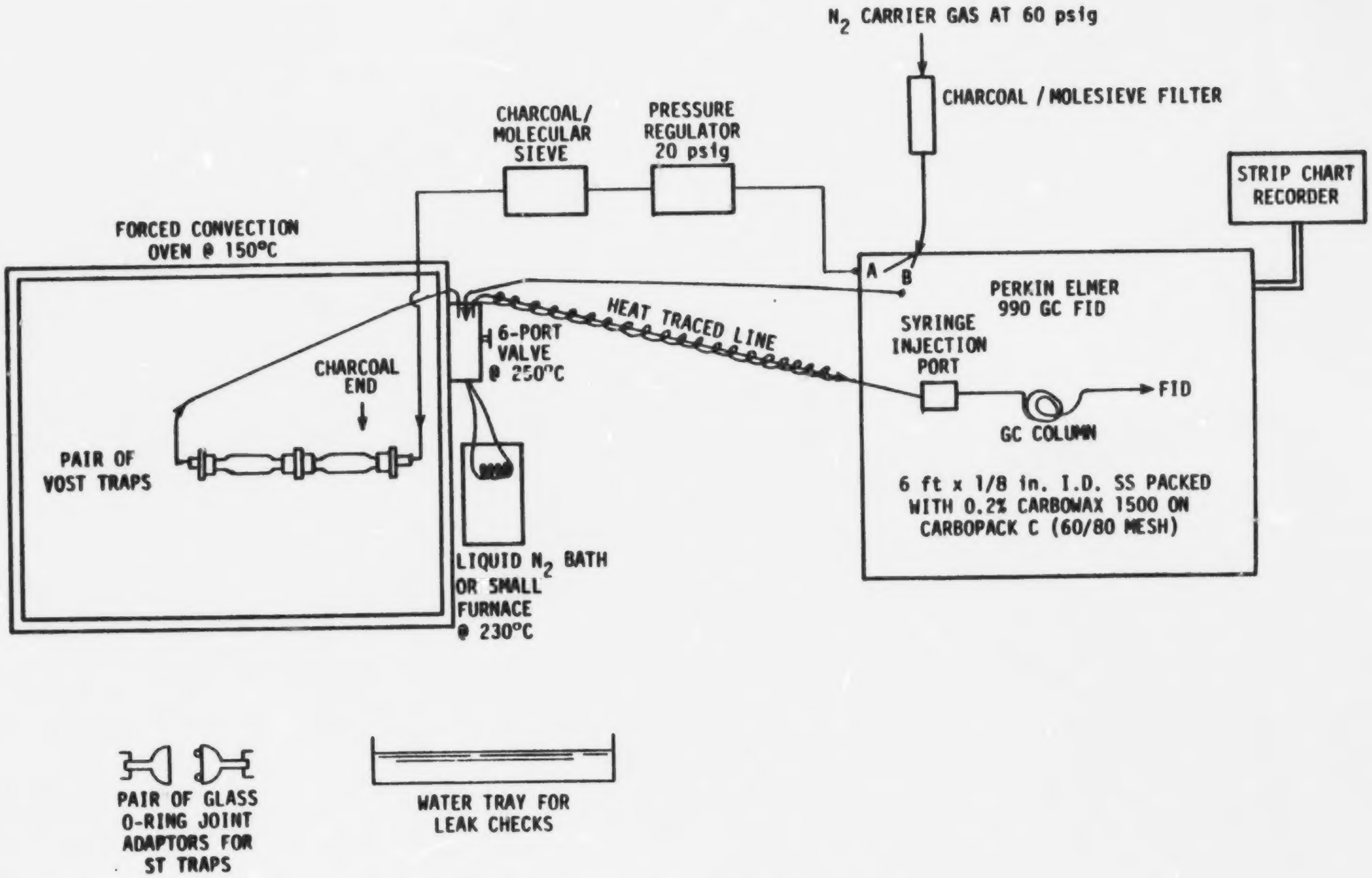
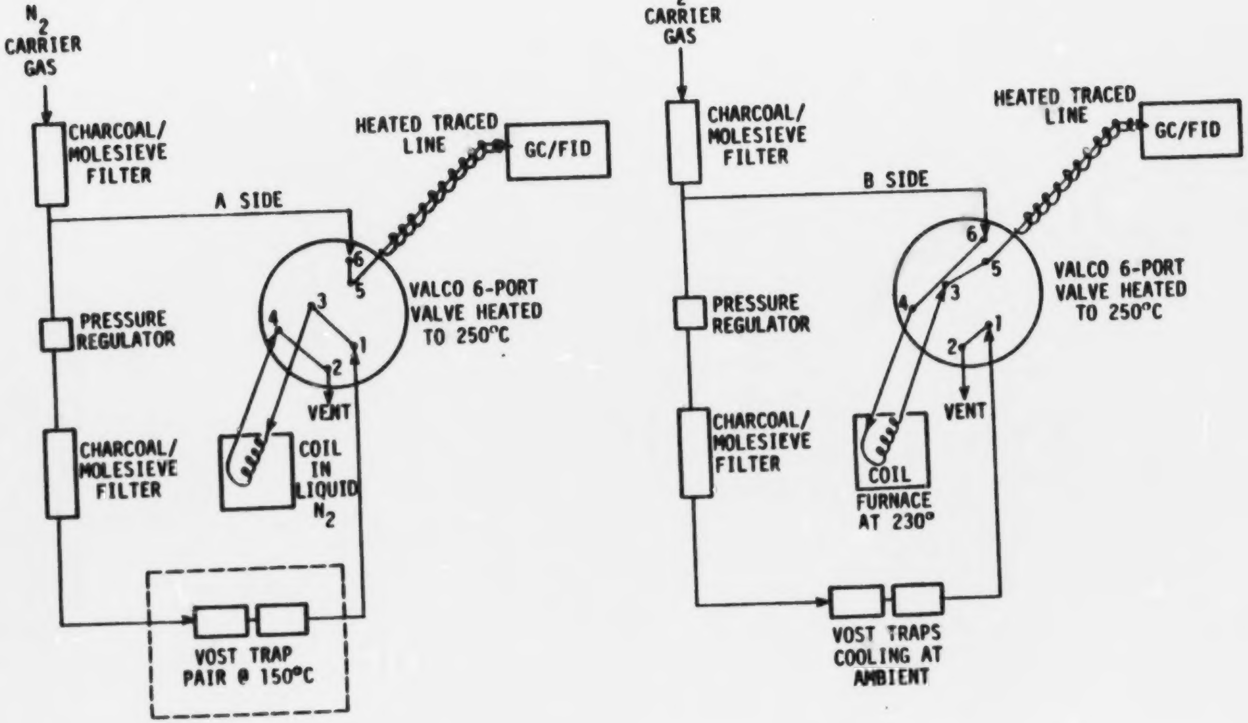

N_2 CARRIER GAS AT 60 psig
CHARCOAL / MOLESIEVE FILTER
CHARCOAL/ MOLECULAR SIEVE
PRESSURE REGULATOR 20 psig
STRIP CHART RECORDER
FORCED CONVECTION OVEN @ 150°C
A
B
PERKIN ELMER 990 GC FID
HEAT TRACED LINE
6-PORT VALVE @ 250°C
CHARCOAL END
SYRINGE INJECTION PORT
FID
GC COLUMN
PAIR OF VOST TRAPS
6 ft x 1/8 in. I.D. SS PACKED WITH 0.2% CARBOWAX 1500 ON CARBOPACK C (60/80 MESH)
LIQUID N_2 BATH OR SMALL FURNACE @ 230°C
PAIR OF GLASS O-RING JOINT ADAPTORS FOR ST TRAPS
WATER TRAY FOR LEAK CHECKS

Figure B-2. Schematic of GC/FID blank-checking system.


N_2 CARRIER GAS
CHARCOAL/ MOLESIEVE FILTER
A SIDE
PRESSURE REGULATOR
CHARCOAL/ MOLESIEVE FILTER
HEATED TRACED LINE
GC/FID
VALCO 6-PORT VALVE HEATED TO 250°C
6
5
4
3
2
1
VENT
COIL IN LIQUID N_2
VOST TRAP PAIR @ 150°C
N_2 CARRIER GAS
CHARCOAL/ MOLESIEVE FILTER
B SIDE
PRESSURE REGULATOR
CHARCOAL/ MOLESIEVE FILTER
HEATED TRACED LINE
GC/FID
VALCO 6-PORT VALVE HEATED TO 250°C
6
5
4
3
2
1
VENT
COIL
FURNACE AT 230°
VOST TRAPS COOLING AT AMBIENT

DESORB TRAPS ONTO COIL

INJECT TO GC/FID

Figure B-3. Flow schematic of GC/FID blank-checking system.

2) The pair was leak-checked at approximately 30 psig by immersing the traps in a pan of distilled water and noting any bubbles. Any leak was corrected.

3) After the leak check, the outlet of the Tenax trap was connected to the system, the cryogenic coil trap was placed in liquid nitrogen, and the six-port valve switch was turned to "desorb." The traps were then placed in the oven and desorbed. The ND traps were desorbed for 10 minutes, whereas the ST traps were desorbed for 15 minutes to provide more time for heat to be transferred through the outer glass trap to the sorbents.

4) After the desorption period, the blank sample was injected to the GC by switching the six-port valve, transferring the trap from the liquid nitrogen to the electric furnace, and starting the GC program.

5) The traps were then removed from the oven and allowed to cool to room temperature before being disconnected from the carrier lines (purged-cooldown).

6) For minimization of ambient contamination, traps were disconnected by the following procedure:

   a) With the carrier gas flow on, the outlet of the Tenax trap was disconnected and capped.

   b) The traps were disconnected in the middle, and both traps were capped.

   c) The Tenax/charcoal trap was then disconnected from the carrier gas line and capped.

7) The ND traps were immediately placed back in their respective culture tubes, which were taped together to keep paired traps as a unit. All traps were stored in refrigerated cans.

Calibration was accomplished by desorbing an ND Tenax trap spiked with a gas standard containing about 20 ng each of benzene and toluene and 65 ng of tetrachloroethylene. The Tenax trap was loaded by injecting the standard into a flash vaporizer purged with nitrogen at 35 ml/min and allowing the gas to purge through the Tenax trap for one full minute.

Gas standards were prepared by injecting pure liquid standards into a 1-liter glass bottle sealed with a "Mininert" valve cap and filled with helium.

Calibration data and blank check activities were documented in a log book. Blank-check data were summarized on blank-check data sheets.

CHARCOAL COMPARISON

After the laboratory evaluation tests were completed, the charcoal preparation procedures were evaluated in an effort to improve blank values of conditioned sorbent traps. A comparison was made between charcoal extracted with methanol and unextracted charcoal. The methanol-extracted charcoal was the same as that used in the laboratory validation tests. The unextracted charcoal came from the same lot of charcoal and was prepared as follows:

- New charcoal was placed in a cylindrical metal container open at the top and connected to a source of charcoal-filtered nitrogen at the bottom. Nitrogen purge flow is set to approximately 50 ml per minute. The charcoal and metal container are placed in a vacuum oven set at 190°C and approximately 5 in. Hg vacuum for a minimum of 6 hours. Cleaned charcoal is transferred to a clean amber glass bottle with a Teflon-lined screw cap and placed in a sealed glass aquarium containing activated charcoal in the VOST preparation room until it is packed in sorbent traps.

Several ND traps were packed with each type of charcoal (no Tenax). These traps were conditioned for a single 28-hour period at 190°C according to the same procedures described earlier. For elimination of potential contamination from airborne materials in the environment, the following additional handling procedures were implemented:

- The culture tubes were first purged with nitrogen before inserting conditioned traps as they were removed from the manifold.
- The storage cans containing a layer of charcoal were also purged with nitrogen before the conditioned traps were inserted.
- The traps were placed in the cans with the culture tube cap facing down (in the charcoal).
- The culture tubes and cans were purged in the same manner after the blank checks.

All of the charcoal traps were blank checked on the GC/FID system as previously described with the following exceptions: a different GC column was used, some of the run times were shortened to 18 minutes, and the calibration standard contained acetone and hexane as well as the other three compounds. By adding acetone and hexane to the standard, the presence of these compounds in the blank sample could be determined by matching retention times.

Before the charcoal traps were blank-checked, a system blank and calibration run were made. Figures B-4 and B-5 are chromatograms from these runs. The system blank was very clean except for the two small peaks early in the run. The calibration run indicates that a response equal to 10 percent of scale represents approximately 3.7 ng as benzene, which is excellent sensitivity.

Figure B-6 is a chromatogram of one of the methanol-extracted charcoal traps, and Figure B-7 is a chromatogram of an unextracted charcoal trap. Both traps are clean, and they are similar except for the large early peak in the chromatogram of the extracted charcoal. This peak is probably methanol or a methanol-related compound. Except for this early peak, which should not interfere with any analyses, the two types of charcoal were essentially the same. These results do indicate that extraction with methanol is not required.

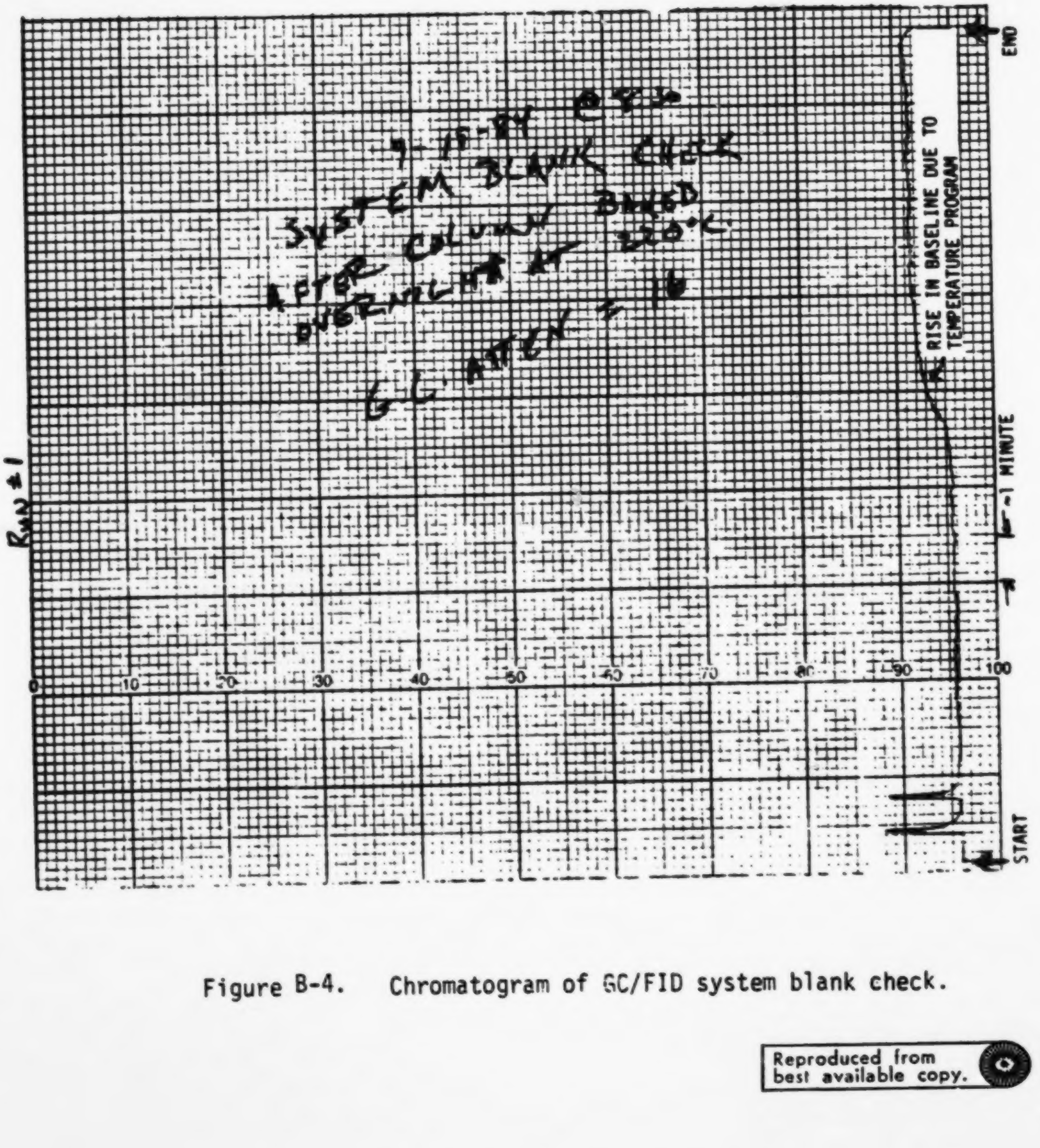


Figure B-4. Chromatogram of GC/FID system blank check.

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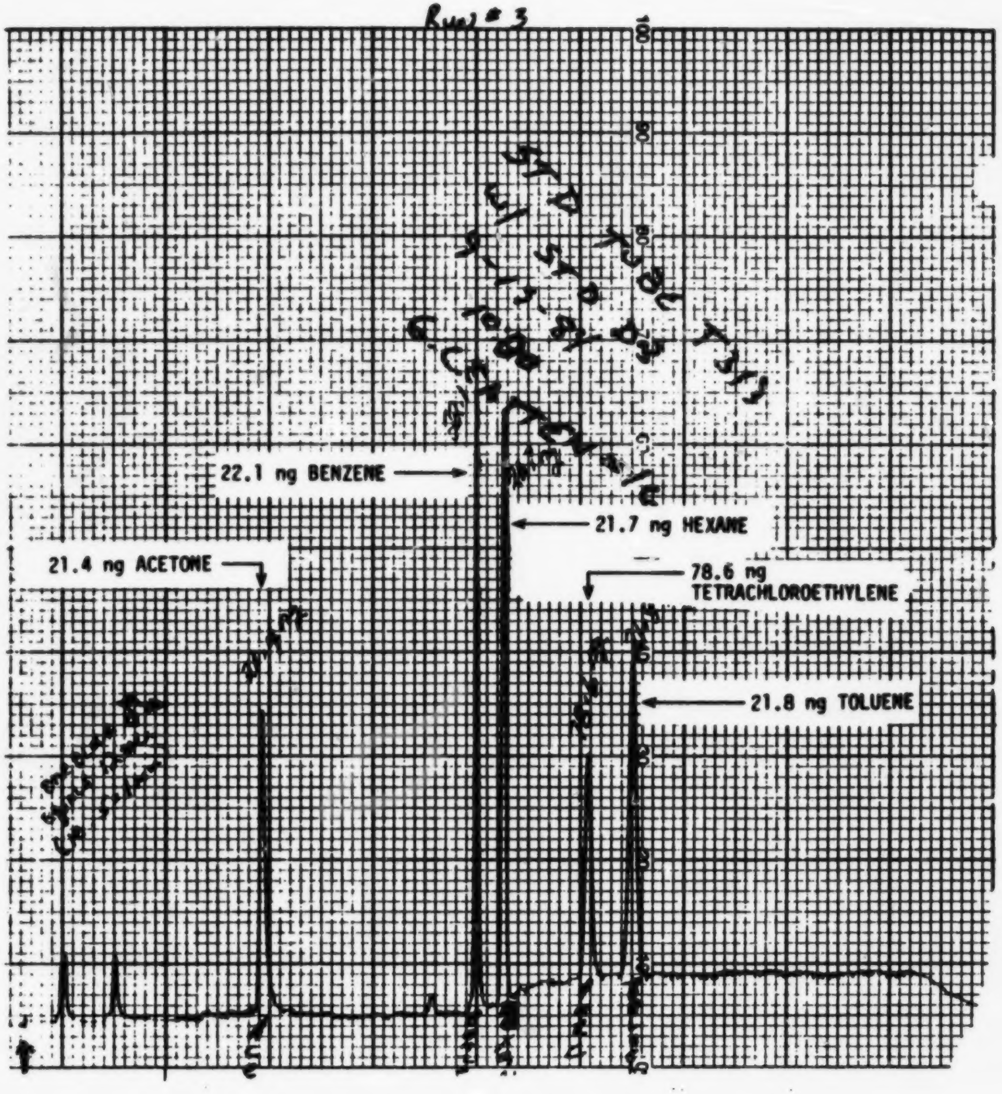

Figure B-5. Chromatogram of GC/FID calibration.

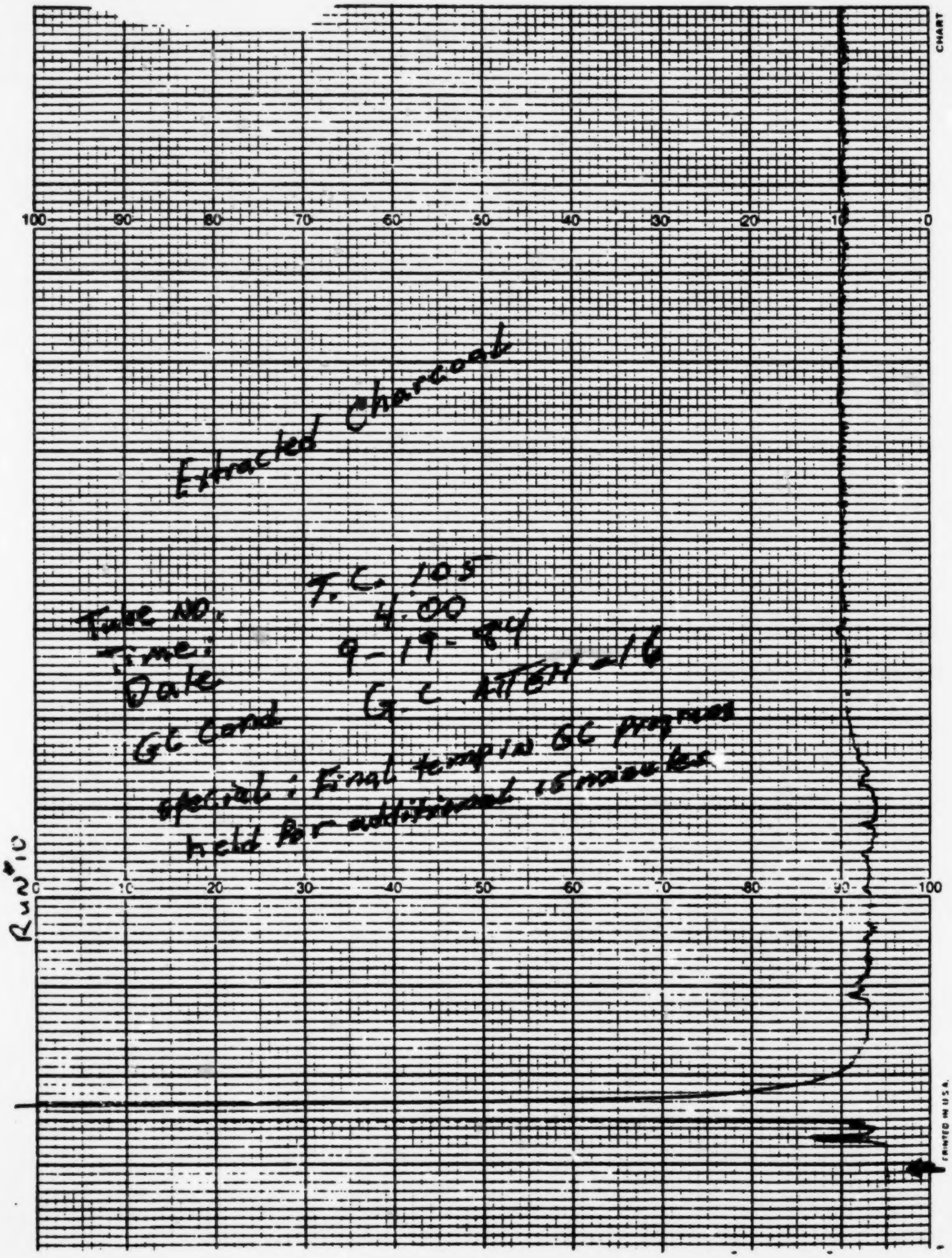

Figure B-6. Blank-check chromatogram of charcoal extracted with methanol.

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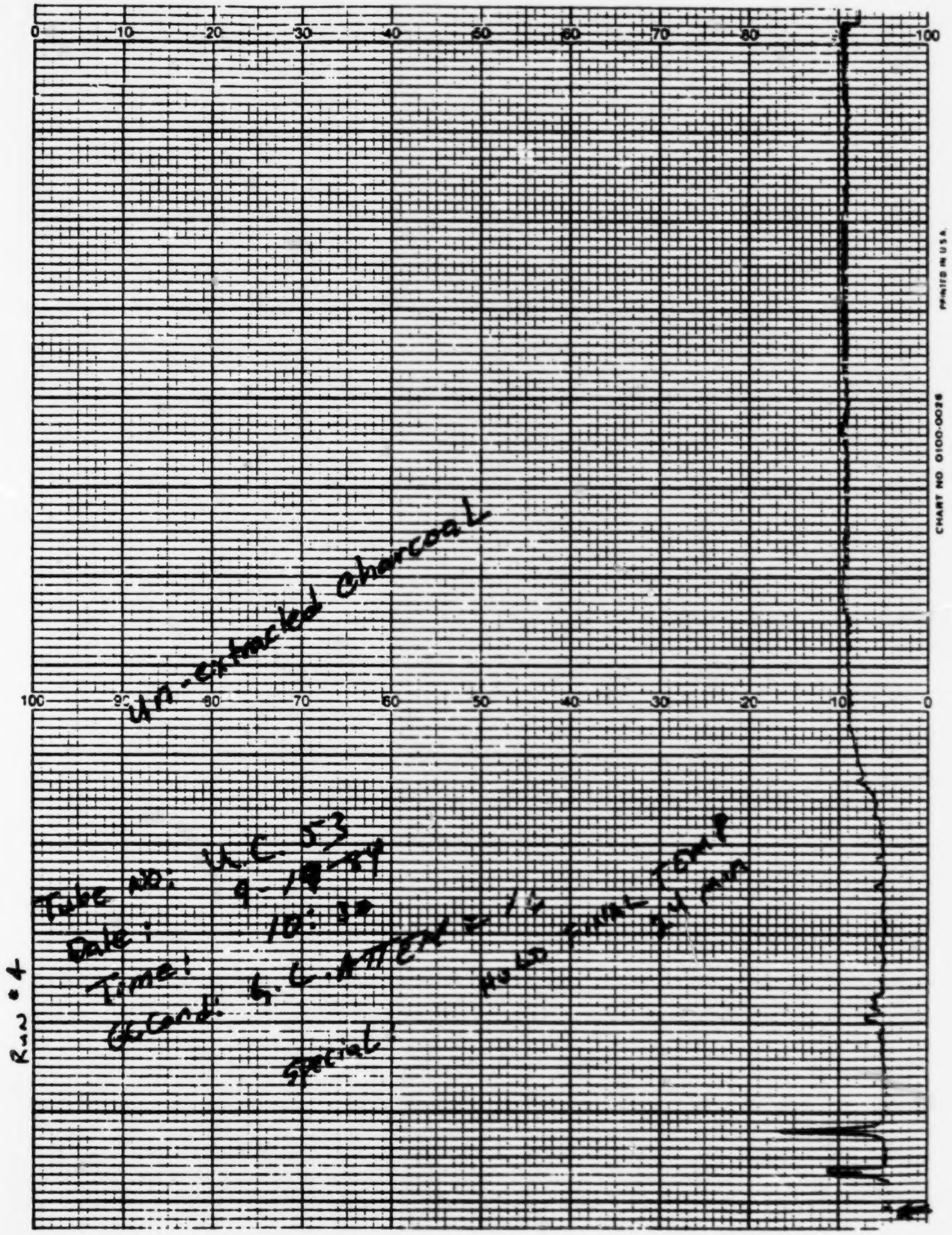

Figure B-7. Blank-check chromatogram of unextracted charcoal.

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APPENDIX C

ANALYTICAL PROCEDURES

ANALYTICAL PROCEDURES

A schematic diagram of the analytical system was shown previously in Figure 3-11. Each sample sorbent trap (either Tenax or Tenax/charcoal) was spiked with an internal standard using a flash vaporization device and thermally desorbed for 10 minutes at 180°C with organic-free helium gas. The gas, which had a flow rate of 40 ml/min, was bubbled through 5 ml of organic-free water and trapped on an analytical sorbent trap. After the 10-minute desorption period, the analytical sorbent trap was rapidly heated to 180°C with the carrier gas flow reversed so that the effluent flow from the analytical trap was directed into the GC/MS. The volatile organics were separated by temperature-programmed gas chromatography and detected by low-resolution mass spectrometry. The mass of each target compound was calculated by the internal standard technique.

APPARATUS

Thermal Desorption Unit

A modified Supelco High-Capacity Gas Purifier Oven ("Clamshell" oven) was used for thermal desorption of ND sample traps. A Variac and thermocouple were used to control and monitor the oven temperatures. A modified Nutech Corporation Model 320 desorber was used for thermal desorption of ST traps. The desorption units were plumbed in parallel with two stainless steel three-way valves to permit analysis of either type of trap.

The desorption gas flow rate was set at about 40 ml/min rather than the 100 ml/min specified in the protocol. (The 100-ml/min rate was probably taken from a previous development report concerning simultaneous desorption of multiple traps.) A rate of 40 ml/min corresponds with Method 624.

The flow path through the Model 320 thermal desorption unit was reversed in our system, and internal plumbing was rerouted so that the purge gas inlet was at the bottom of the desorption chamber and the outlet was on the side near the top (see Figure 3-11). In the standard unit, the purge gas enters at the side near the top and exits at the bottom. In the Model 320, the gas exiting the desorption chamber passes through an internal six-port valve and coil of tubing that can be used as a cryogenic trap. We reversed the gas flow through the desorption chamber to avoid potential problems caused by loose Tenax particles falling down and being forced into the bottom opening into the six-port desorber valve and causing plugging or damage to the valve. During the VOST analysis, the six-port valve was left in one position so that the sample-containing desorption gas passed through the six-port valve, on through the coil trap (which was maintained at approximately 180°C), and out of the desorber unit. The six-port valve and coil trap serve no useful purpose in the VOST analysis and could be replaced with a section of heated tubing to minimize potential operating problems.

The protocol mentions the option of analyzing sample sorbents singly; e.g., analysis of a Tenax trap followed by analysis of the corresponding Tenax/charcoal trap, or as a pair (i.e., the Tenax and Tenax/charcoal traps are connected in series and analyzed as one unit). With the equipment described in the protocol and that used for PEI's work, only the ND traps could be analyzed as a pair. The Model 320 desorber used for the ST traps holds only one trap at a time. Thus, the ST traps cannot be analyzed as a pair unless they are sequentially desorbed onto the analytical trap. This would not be valid, however, because the ST Tenax and Tenax/charcoal traps yield different calibration response curves for some compounds.

The protocol also mentions an optional technique of increasing method sensitivity by desorption of multiple pairs of sample traps onto a single pair of traps for subsequent analysis. No equipment or procedures are described for doing this, however.

The laboratory study sample traps were analyzed singly, except in several instances which are noted.

Purge and Trap Unit

The purge and trap unit was a Tekmar Model LSC-2, on which all Teflon transfer lines were replaced with 1/16-in. o.d. stainless steel tubing to avoid contamination and/or losses. The protocol did not specify the materials to be used in transfer lines to, from, and within the purge and trap unit. PEI's experience has indicated, however, that Teflon is a poor choice for such lines because Teflon can absorb many volatile compounds. The internal volume of the glass purge vessel was approximately 25 ml, and it contained 5 ml of organic-free water.

The internal analytical trap consisted of a 15-cm long section of Tenax, a 3.7-cm section of silica gel, and a 3.7-cm section of charcoal. The protocol indicated the analytical trap configuration should be "as specified in EPA Method 624*"; however, the detailed component information given in the protocol was for the trap used in Method 601, not the one in Method 624. The Method 601 trap is similar to the one just described except that it contains a section of methyl silicone packing in front of the Tenax, and is thus a four-component trap. Communications with several other laboratories conducting VOST analyses indicated that various analytical traps were being used. Of the nine laboratories contacted, three reported they used the four-component Method 601 trap, one used a Tenax/silica gel/charcoal trap, three used traps containing Tenax and silica gel, and two used traps consisting only of Tenax. Upon inquiry, the Tekmar Company (a common supplier of purge and trap devices and traps) stated that they have never produced a four-component trap and that the standard trap they sell for Method 624 contains the same material as indicated for the three-component trap PEI used.

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*EPA Test Method "Purgeables - Method 624," U.S. EPA, EMSL, July 1982.

Because the protocol did not specify any particular criteria for trap recovery (an overall system recovery is specified, however) and because of the broad range of traps typically used, selection of a trap for the validation study was based on a preliminary recovery study. Trap recovery was determined by comparing the GC/MS area response of gas standard mixtures injected at the head of the GC column (i.e., after the trap) by means of a septum tee fitting and at the purge vessel (i.e., in front of the trap). Purposely excluding the effect of sample trap desorption or water purging efficiency in this recovery check enabled us to evaluate only the effect of the analytical trap under prescribed system operating conditions. A Tenax/charcoal trap we had used in previous VOST work and a commercially available Tenax/silica gel/charcoal trap were evaluated by the use of the six target compounds and a hexafluorobenzene (HFB) internal standard. Approximately 500 ng of each target compound and 1300 ng of HFB were injected three times before and after the trap. Results are shown in Table C-1.

TABLE C-1. TRAP RECOVERY CHECKS
(average percent recovery and relative standard deviation)

Trap	Vinyl chloride	TCFM	Chloroform	Carbon tet	Benzene	Perc	HFB
Tenax/charcoal	116 ± 3	106 ± 2	99 ± 2	99 ± 1	98 ± 1	102 ± 2	109 ± 6
Tenax/silica gel/charcoal	111 ± 3	100 ± 3	96 ± 3	99 ± 3	97 ± 2	100 ± 2	106 ± 3

The results for HFB are based on area responses of HFB. Results for the target compounds are based on the ratio of area response between the compound and HFB. Finding essentially no difference in trap performance, we decided to use the commercially available three-component trap from Tekmar for the remainder of the laboratory validation. The protocol should specify a procedure and criteria for evaluating whether a particular trap configuration performs acceptably for a given application.

The purge and trap device used was a commercially available device manufactured to meet the requirements of Method 624, as specified in the protocol except for the specific trap materials just described.

GC/MS System

The GC/MS system used was a Finnigan Model 4023 with quadrupole mass spectrometer. The temperature-programmable gas chromatograph included a septum-plugged tee fitting through which "on-column" injections could be made for recovery and tune checks.

The glass column was 6 feet by 2 mm i.d. and packed with 1 percent SP-1000 on Carbopak B (60/80 mesh). Because glass columns are not available in the 0.25-cm i.d. specified, the protocol specification should read, "Column dimensions shall be 1.8 m long by 2.5 mm i.d. for stainless steel or 2.0 mm i.d. for glass."

The protocol specifies only one GC column packing material (1% SP-1000 on Carbopak B 60/80 mesh or equivalent). This may not allow the analyst sufficient flexibility in choice of column to assure the accomplishment of adequate separations in all applications. Some criterion should be given for evaluating an alternate column. This would give the analyst enough flexibility in column choice to permit proper resolution of target compounds, internal standard(s), and matrix compounds so that valid qualitative identifications can be made with minimal mass spectral overlap. The following is an example of such a criterion found in Method 624, Section 12.2, for evaluating resolution between structural isomers: "Acceptable resolution is achieved if the baseline to valley height between the isomers is less than 25 percent of the sum of the two peak heights."

Operating conditions for suitable chromatography were determined by analysis of preliminary samples. The temperature program was set at 50°C for 2 minutes, ramped at 10° per minute up to 220°C, and held for 1 minute to yield a total run time of 20 minutes.

The GC to MS interface was an all-glass jet separator. The mass spectrometer was scanned from 35 to 335 m/e (mass to charge ratio) every 2 seconds. The protocol specifies that the mass spectrometer be capable of scanning the mass range from 20 to 260 amu every 7 seconds or less, but it does not specify or recommend a mass scanning range or rate to be used for sample analysis. The mass spectrometer could not be scanned as low as 20 m/e because of the large response to methanol (molecular ion = 32 m/e) solvent used to load the internal standards. Oxygen and nitrogen would also give large responses when scanning down to 20 m/e, but these might not disrupt the chromatogram as badly as methanol, as methanol is more likely to "tail" than the permanent gases.

The mass spectrometer was set to operate in the electron impact mode at 70 electron volts (nominal). The preamplifier (electrometer range) was set at 10^{-7} amperes per volt (amps/v) for all analyses. A setting of 10^{-8} amps/v was used for the GC/MS performance tune checks to obtain complete spectral information. Two electron multiplier voltage settings were used during the laboratory study to modify detector sensitivity so that the range of expected target compound levels would be within the linear working range of the instrument. A setting of 1500 volts was used during the weeks when low-level samples were analyzed, and 1300 volts were used for high-level samples.

The data acquisition and processing system that controlled the mass spectrometer consisted of a Data General Nova 3 computer with a Perkin-Elmer/Wangco 10-megabyte dual-disk drive that runs Finnigan Incos Software. This system permitted continuous acquisition and storage of all mass spectra obtained during chromatographic analyses. It also permitted the searching of data files for ions of selected masses and the searching of certain scans for comparison to the NBS library of mass spectra for best matches. It also permitted plots and integrations of peak areas of Extracted Ion Current Profiles.

REAGENTS

Desorber Gas

Helium was used as the thermal desorption gas, instead of nitrogen as specified in the protocol, because some of the sample trap desorption gas is backflushed into the GC when the analytical trap is being desorbed. Helium behaves better than nitrogen in the glass jet separator because it is more easily removed from the sample stream and it produces adiabatic heating at the jet tip, whereas nitrogen would cause cooling. Cooling might cause sample condensation or, more likely, condensation of any liquid phase bleeding off of the column.

Analytical Traps

Preliminary recovery checks--

Tenax/charcoal - Chromatographic grade Tenax (60/80 mesh); petroleum-based charcoal (Calgon type GW 20 x 50).

Sample analysis--

Tenax/silica gel/charcoal - Tekmar part No. 14-0124-003.

Reagent Water

Reagent water, defined as water in which an interference is not observed at the detection limit of the parameters of interest, was generated by passing deionized water through a carbon filter bed and then boiling it for 15 minutes. While still hot, the water was transferred to a sealed syringe for loading into the analytical purge vessel.

Target Compound Standard Materials

Neat liquid calibration standards from commercial suppliers were used for five of the target compounds; this was compatible with the method the protocol specified for preparing standard solutions in methanol. The purity of all liquid standards was checked by GC/MS analysis at the beginning of the study. Aliquots of gas bottle standards prepared from the liquid standard were injected on column with an internal standard. Approximate purities were calculated by dividing the area response of the target compound by the total area response of the run (except for the air and internal standard peaks). The results are shown in Table C-2.

TABLE C-2. PURITY OF LIQUID CALIBRATION MATERIALS
(area percent)

TCFM	Chloroform	Carbon tetrachloride	Benzene	Perc
100.0	99.3	99.6	99.6	99.9

The low boiling point of vinyl chloride (VC) precluded the use of a liquid standard; in fact, a pure calibration standard of VC in liquid or gas form generally cannot be obtained because of limited supply. Once distributors of calibration materials consume their existing supplies of pure VC, they may not be able to get any more. Therefore, it was decided to use a gas cylinder mixture (30.6 ppm VC in nitrogen) from EPA's repository of audit materials as a calibration standard. Syringe aliquots were taken from the cylinder for GC/MS calibration. This deviation from the VOST protocol (use of a gas standard) was necessary if VC was to be included in the validation. Other VC calibration materials (e.g., permeation tubes) could have been used, but they did not adapt well to the methanolic standard loading techniques used for the other compounds. The cylinder concentration of VC had been verified previously by independent analyses by RTI and the National Bureau of Standards (NBS). Prior work by RTI associated with EPA's audit program had also shown the cylinder to be stable (±10%); therefore, the cylinder was not reanalyzed after the study.

Standard Solutions

Fresh stock standard solutions were prepared weekly by mixing aliquots of the five liquid standard materials in Burdick and Jackson glass-distilled methanol. Secondary dilution standards in methanol were prepared from the stock standards at concentrations that would allow equal volumes (approximately 4 µl) of the desorbed calibration standards to bracket the range of expected sample concentrations.

The protocol requires methanolic standard solutions. Because of the potential problems with methanol (e.g., limitations on low mass scan range, possible reactivity, and the impracticality of creating methanolic standards of very low boiling point compounds), the use of alternative standards should be considered. Such alternatives should include:

- Static gas bottle standards
- Gas cylinder standards
- Permeation devices

These alternatives to methanolic standards might permit scanning the MS from as low as 20 m/e which would provide more complete spectra of low-molecular-weight volatile compounds. This could improve the quality of some spectral library search results and qualitative identifications.

Bromofluorobenzene (BFB) Standard--

A solution of 50 µg/ml BFB in methanol was prepared. One microliter of this standard was injected on column each day for MS tune checking.

Internal Standards--

Solutions of d_6-benzene and hexafluorobenzene in methanol usually were prepared weekly at a concentration that would allow a 4-µl injection to produce an amount on column in the mid-range of the expected amounts of target compounds.

The protocol specifies that each sorbent trap be spiked with 50 ng of a single internal standard (deuterated benzene) in methanol. More flexibility should be permitted for standard preparation. The internal standard amount(s) loaded on each trap should be in the mid-range of expected target compound amounts. Also, more than one internal standard may be needed depending on the specific compounds of interest. The selected internal standard(s) should be a deuterated volatile compound(s) that can be chromatographically separated from all target compounds and major matrix interferences. At least three deuterium atoms should be substituted on the molecule to separate the mass spectral clusters of the parent and deuterated compound. No internal standard should be a deuterated homolog of a target analyte (e.g., d_6-benzene and benzene) because their coelution may preclude qualitative identification of the target compound at low levels relative to the internal standard. Also, quantitative interference may result when a minor ion from the deuterated internal standard coincides with the quantitation ion of the target compound. As indicated in the protocol, the important criterion for selecting an internal standard(s) is that its analytical behavior be similar to that of the target compound(s).

PEI chose hexafluorobenzene for use in this study, in addition to d_6-benzene, because of our past frequent usage of this compound as an internal standard for Tenax analyses. There were no major problems associated with the use of HFB; however, a more volatile deuterated compound should be selected for future analyses involving TCFM or VC.

The protocol does not specify whether the internal standard should be included in the same methanol solutions as the mixtures of target compounds. In this study, the internal standards were prepared in a separate methanolic solution. This permitted the same internal standard solution to be used to spike the calibration sorbent traps as well as the sample traps, which eliminated any possible error associated with making up several internal standard solutions (one for spiking samples and one mixed with each calibration solution).

DAILY GC/MS PERFORMANCE TESTS

Daily GC/MS performance tests were conducted by injecting 50 ng of BFB directly on the column. The key ion abundance criteria for BFB that were met before any samples or blanks were analyzed are listed in Table C-3.

TABLE C-3. BFB KEY ION ABUNDANCE CRITERIA

Mass	Ion abundance criteria
50	15 to 40% of mass 95
75	30 t0 60% of mass 95
95	Base peak, 100% relative abundance
96	5 to 9% of mass 95
173	<2% of mass 174
174	>50% of mass 95
175	5 to 9% of mass 174
176	>95% but <101 of mass 174
177	5 to 9% of mass 176

Table C-4, which summarizes the GC/MS performance data obtained during the laboratory study, shows that the criteria were met each day of analysis. As previously noted, the MS electrometer range was set to 10^{-8} amp/v for the performance test to obtain the necessary spectral information for low-abundance ions. The samples were run at an electrometer setting of 10^{-7} amp/v because there was less signal noise than at 10^{-8} amp/v. This is routine procedure.

GC/MS CALIBRATION

Calibration and internal standards were loaded onto the sorbent traps by use of the flash evaporation apparatus previously shown in Figure 3-12. The apparatus used consisted of two identical glass evaporation chambers with septum-plugged side arms for injection. These chambers were both connected to a source of nitrogen (from a gas cylinder) via a three-way switching valve. Both glass chambers were heated to about 150°C with heating tape.

TABLE C-4. GC/MS PERFORMANCE DATA
(percentage abundance at indicated ions)

Date (1984)	Ions (criteria in parentheses)								
	50 (15-40% of ion 95)	75 (30-60% of ion 95)	95 (100%)	96 (5-9% of ion 95)	173 (<1% of ion 95)	174 (>50% of ion 95)	175 (5-9% of ion 174)	176 (>95%, <101% of ion 174)	177 (5-9% of ion 176)
4/23	20	43	100	6	-	79	6	95	5
4/24	20	39	100	9	-	79	7	97	7
4/25	21	40	100	8	-	85	7	98	6
4/26	24	41	100	6	-	89	6	99	6
4/30	24	43	100	11	-	89	7	97	6
5/1	25	41	100	9	1	85	7	96	6
5/2	22	39	100	9	-	82	6	99	6
5/3	16	42	100	7	-	84	6	96	5
5/7	24	38	100	6	-	82	6	100	5
5/8	23	39	100	7	-	87	7	98	6
5/9	26	39	100	7	-	85	7	96	6
5/10	26	40	100	7	-	85	7	97	6
5/11	23	42	100	7	-	85	6	99	6
5/14	22	40	100	7	-	88	7	97	6
5/15	23	39	100	6	-	85	7	100	6
5/16	22	40	100	7	-	85	6	96	6
5/17	22	37	100	6	-	87	6	99	5
5/18	17	39	100	6	-	85	6	96	5
5/21	21	38	100	6	-	91	6	99	5
5/22	15	41	100	6	-	84	6	98	5
5/23	16	40	100	6	-	82	6	100	5
5/24	24	50	100	6	-	60	8	101	7
5/25	22	49	100	6	2	91	7	96	6
5/29	18	45	100	6	-	87	6	97	6

(continued)

TABLE C-4 (continued)

Date (1984)	Ions (criteria in parentheses)								
	50 (15-40% of ion 95)	75 (30-60% of ion 95)	95 (100%)	96 (5-9% of ion 95)	173 (<1% of ion 95)	174 (>50% of ion 95)	175 (5-9% of ion 174)	176 (>95%, <101% of ion 174)	177 (5-9% of ion 176)
5/30	16	33	100	8	-	91	7	96	7
5/31	23	43	100	6	1	84	6	98	6
6/1	18	48	100	5	-	82	6	97	5
6/4	26	42	100	7	-	91	7	95	5
6/5	29	43	100	6	-	86	7	97	6
6/6	26	44	100	7	-	85	7	96	6
6/7	24	42	100	6	1	83	6	99	6
6/8	24	41	100	6	1	86	6	100	6
6/11	19	46	100	6	-	82	6	99	6
6/12	21	44	100	6	-	80	6	100	6
6/13	17	55	100	7	-	91	6	98	6
6/14	18	46	100	6	1	86	6	96	6
6/15	18	55	100	5	1	76	6	101	5
6/18	25	42	100	6	-	83	6	99	6
6/19	24	43	100	6	-	89	6	98	6
6/20	23	42	100	6	1	86	7	96	5
6/21	17	44	100	6	-	86	5	98	5
6/22	27	42	100	6	-	81	6	99	6
6/26	24	42	100	6	-	87	6	96	6
6/27	25	44	100	6	1	85	6	100	5

Appropriate brass and stainless steel adaptor fittings with Teflon ferrules were connected to the ¼-in. o.d. tube outlet of one chamber to allow it to accept the 16-mm o.d. ST traps. The other chamber was connected to the ND traps with a ¼-in. union and Supeltex M-1 ferrules. Carrier flow was set at 100 ml/min so that either chamber volume (approximately 25 ml) was well swept in a 1-minute loading interval.

An alternative flash evaporation chamber could consist of a heated, stainless steel tee pitting with a septum in one port. The small volume of such a device would permit the use of a small gas volume to flush the standard onto the trap.

Initially, the adaptor fitting used to connect ST traps to the flash evaporation device was all Teflon; however, preliminary calibrations yielded erratic results for vinyl chloride and tetrachloroethylene. Our suspicion that these compounds were being adsorbed by the large body of Teflon in the adaptor was apparently proved correct when the problem was eliminated by replacing the Teflon adaptor with a brass one (except for the Teflon ferrules).

As specified in the protocol, the "solvent flush" technique was used to load methanolic standards. In this study the internal standards were prepared in a separate methanolic solution. Simultaneous injection of both internal standard and target compound calibration standard aliquots was accomplished as follows: about 1 µl of methanol was pulled into a 10-µl syringe for solvent flush, followed by an air space, a 4-µl target compound aliquot, an air space, a 4-µl aliquot of the internal standard, and a final air space. Both standard aliquots were measured by difference in the syringe barrel markings. The entire contents of the syringe were then injected into the flash-evaporation chamber. The methanolic injection was immediately followed by an injection of a gaseous (30.6 ppm in N_2) vinyl chloride standard. The vinyl chloride gas standard aliquots were withdrawn from a dynamic flow of gas from the calibration gas cylinder. A gas-tight syringe was inserted into a tee fitting equipped with a septum plug to withdraw a standard vinyl chloride aliquot (as shown previously in Figure 3-13). A total of 100 ml of carrier gas was passed through the chamber and trap after the VC injection. Sample traps were loaded in a similar manner except that only the internal standard was loaded.

Calibration Levels

The three-point high-range calibration curve for the 15-ppb samples was generated by using standards nominally containing 2500, 1200, and 500 (or 250) ng of each target. The low-range curve for 0.5-ppb samples was generated by using nominal standards of 500 (or 250), 100, and 20 ng. Internal standard levels differed for each curve; they were nominally 1000 ng for the high-range curves and 250 ng for the low-range curves.

Types of Calibration Curves

Because the calibration responses among ST-T, ND-T, and ND-TC trap types were similar as discussed in Section 3, one calibration curve per target compound was used to represent all three traps, and a separate curve was used to represent the ST-TC traps. A three-point (minimum) calibration curve was generated at the beginning of each test week (either high- or low-range, as appropriate) for ST-TC traps. A second curve was generated for the other three trap types. A different trap type was used to generate the three-trap curve each week, but all three points in a given week's curve were made with one type of trap.

After a sorbent trap was loaded with calibration standards, the trap was desorbed and analyzed as a sample. The area responses of the characteristic ion of each analyte (target compound) and internal standard (IS) were tabulated with their respective amounts loaded. A response factor (RF) was calculated for each compound versus its internal standard by using Equation C-1.

$$RF = A_s C_{is} / A_{is} C_s \qquad \text{(Eq. C-1)}$$

where A_s = area of the characteristic ion for the analyte to be measured

A_{is} = area of the characteristic ion for the internal standard

C_{is} = amount (ng) of the internal standard

C_s = amount (ng) of the volatile analyte in calibration standard

The characteristic ions used for each target and internal standard were listed previously in Table 3-4. A computer-generated quadratic-fit curve to the calibration points of A_s versus RF was used in the laboratory study for each target compound.

Calibration Checks

The weekly calibration curves were updated on each working day by the analysis of one or more of the calibration standards. The daily check-point standard was added to the previous calibration data, and a revised curve was generated for that day's analysis. The ST-TC traps were always used for the ST-TC curves; however, the type of trap used to update the three-trap curve (ND-T, ND-TC, and ST-T) was varied each day to ensure representativeness.

Daily checks of calibration response factors made during the laboratory study are presented in Tables C-5 (for the ND-T, ND-TC, and ST-T traps) and C-6 (for ST-TC traps). In Table C-5 the types of traps used to generate the initial weekly curve are identified, as well as the type of trap used to make

TABLE C-5. SUMMARY OF GC/MS DAILY RESPONSE FACTOR CHECKS ON COMBINED CALIBRATION CURVE FOR ND-T, ND-TC, AND ST-T TRAPS

	Compound			Vinyl chloride			TCFM			Chloroform			Carbon tetrachloride			Benzene			Tetrachloroethylene		
	Trap type		Nominal calib. pt., ng	Response factors		% Difference	Response factors		% Difference	Response factors		% Difference	Response factors		% Difference	Response factors		% Difference	Response factors		% Difference
Date (1984)	Initial	Daily check		Initial	Daily check		Initial	Daily check		Initial	Daily check		Initial	Daily check		Initial	Daily check		Initial	Daily check	
4/23	ND-T	ND-T	250[a]	0.536	0.784	46.3	0.773	0.748	-3.2	0.702	0.672	-4.3	0.464	0.431	-7.1	1.040	0.989	-4.9	0.534	0.504	-5.6
4/24	ST-T	ST-T	250[a]	1.004	0.858	-14.5	0.809	0.808	-0.1	0.750	0.757	0.9	0.522	0.526	0.8	1.043	1.161	11.3	0.480	0.448	-6.7
4/26	ST-T	ST-T	250[a]	1.004	0.812	-19.1	0.809	0.877	8.4	0.750	0.780	4.0	0.522	0.621	19.0	1.043	1.022	-2.0	0.480	0.489	1.9
5/1	ND-T	ST-T	250	-	b	-	0.437	0.405	-7.3	0.515	0.531	3.1	0.285	0.276	-3.2	1.041	1.023	-1.7	0.494	0.422	-14.6
5/2	ND-T	ND-TC	250	0.754	0.770	2.1	0.437	0.455	4.1	0.515	0.530	2.9	0.285	0.281	-1.4	1.041	1.037	-0.4	0.494	0.513	3.8
5/8	ND-T	ND-TC	1200	0.732	0.758	3.6	0.509	0.512	0.6	0.475	0.501	5.5	0.273	0.285	4.4	1.020	1.042	2.2	0.444	0.473	6.5
5/8	ST-T	ND-TC	1200	0.884	0.758	14.2	0.492	0.512	4.1	0.507	0.501	-1.2	0.274	0.285	4.0	0.988	1.042	5.5	0.356	0.473	32.9
5/9	ND-T	ST-T	1200	0.732	0.826	12.8	0.509	0.541	6.3	0.475	0.516	8.6	0.273	0.298	9.2	1.020	1.008	-1.2	0.444	0.386	-13.1
5/9	ST-T	ST-T	1200	0.884	0.826	-6.6	0.492	0.541	10.0	0.507	0.516	1.8	0.274	0.298	8.8	0.988	1.008	2.0	0.356	0.386	8.4
5/10	ND-T	ND-T	1200	0.732	0.684	-6.6	0.509	0.521	2.4	0.475	0.525	10.5	0.273	0.291	6.6	1.020	1.067	4.6	0.444	0.494	11.3
5/10	ST-T	ND-T	1200	0.884	0.684	-22.6	0.492	0.521	5.9	0.507	0.525	3.6	0.274	0.291	6.2	0.988	1.067	8.0	0.356	0.494	38.8
5/11	ND-T	ND-TC	1200	0.732	0.321	-56.1	0.509	0.394	-22.6	0.475	0.436	-8.2	0.273	0.268	-1.8	1.020	0.898	-12.0	0.444	0.501	12.8
5/11	ST-T	ND-TC	1200	0.884	0.321	-63.7	0.492	0.394	-19.9	0.507	0.436	-14.0	0.274	0.268	-2.6	0.988	0.898	-9.1	0.356	0.501	40.7
5/15	ST-T	ND-TC	100	0.640	0.538	-15.9	0.319	0.295	-7.5	0.573	0.570	-0.5	0.209	0.227	8.6	1.024	1.066	4.1	0.533	0.656	23.1
5/22	ND-T	ND-TC	1200	0.762	0.763	0.1	0.557	0.578	3.8	0.491	0.501	2.0	0.275	0.302	9.8	1.000	1.011	1.1	0.474	0.478	0.8
5/23	ND-T	ST-T	1200	0.762	0.604	-20.7	0.557	0.623	11.8	0.491	0.528	7.5	0.275	0.297	8.0	1.000	0.990	-1.0	0.474	0.390	-17.7
5/24	ND-T	ND-T	1200	0.762	0.820	7.6	0.557	0.537	-3.6	0.491	0.508	3.5	0.275	0.281	2.2	1.000	1.034	3.4	0.474	0.490	3.4
5/25	ND-T	ND-TC	1200	0.762	0.769	0.9	0.557	0.559	0.4	0.491	0.538	9.6	0.275	0.306	11.3	1.000	1.040	4.0	0.474	0.489	3.2
5/30	ND-TC	ND-T	100	0.657	0.623	-5.2	0.492	0.459	-6.7	0.576	0.549	-4.7	0.243	0.222	-8.6	1.137	1.098	-3.4	0.572	0.544	4.9
5/31	ND-TC	ST-T	100	0.657	0.606	-7.8	0.492	0.519	5.5	0.576	0.616	6.9	0.243	0.255	4.9	1.137	1.070	-5.9	0.572	0.487	-14.9
6/1	ND-TC	ND-TC	100	0.657	0.646	-1.7	0.492	0.418	-15.0	0.576	0.615	6.8	0.243	0.246	1.2	1.137	1.100	-3.2	0.572	0.583	1.9
6/5	ST-T	ND-T	100	0.620	0.742	19.7	0.604	0.589	-2.5	0.693	0.688	-0.7	0.219	0.313	7.6	1.081	1.103	2.0	0.508	0.622	22.4
6/6	ST-T	ND-TC	100	0.620	0.625	0.8	0.604	0.474	-21.5	0.693	0.683	-1.4	0.291	0.304	4.5	1.081	1.134	4.9	0.508	0.634	24.8
6/7	ST-T	ND-TC	100	0.620	0.642	3.5	0.604	0.620	2.6	0.693	0.751	8.4	0.291	0.369	26.8	1.081	1.254	16.0	0.508	0.678	33.5
6/8	ST-T	ST-T	20	0.497	0.410	-17.5	0.452	0.417	-7.7	0.692	0.747	7.9	0.207	0.220	6.3	0.984	1.072	8.9	0.430	0.436	1.4

(continued)

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TABLE C-5 (continued)

Date (1984)	Compound			Vinyl chloride			TCFM			Chloroform			Carbon tetrachloride			Benzene			Tetrachloroethylene		
	Trap type		Nominal calib. pt., ng	Response factors		% Difference	Response factors		% Difference	Response factors		% Difference	Response factors		% Difference	Response factors		% Difference	Response factors		% Difference
	Initial	Daily check		Initial	Daily check		Initial	Daily check		Initial	Daily check		Initial	Daily check		Initial	Daily check		Initial	Daily check	
6/12	ND-T	ND-TC	1000	0.676	0.733	8.4	0.643	0.646	0.5	0.592	0.620	4.7	0.371	0.396	6.7	1.081	1.107	2.4	0.565	0.572	1.2
6/12	ND-T	ST-T	2500	-	b	-	0.571	0.619	8.4	0.556	0.598	7.6	0.358	0.386	7.8	1.056	1.074	1.7	0.511	0.426	-16.6
6/13	ND-T	ST-T	2500	0.652	0.591	-9.4	0.571	0.597	4.6	0.556	0.568	2.2	0.358	0.381	6.4	1.056	1.034	-2.1	0.511	0.450	-11.9
6/13	ND-T	ND-T	2500	0.652	0.602	-7.7	0.571	0.500	-12.4	0.556	0.535	-3.8	0.358	0.349	-2.5	1.056	1.039	-1.6	0.511	0.555	8.6
6/13	ND-T	ND-TC	250	0.726	0.734	1.1	0.591	0.536	-9.3	0.666	0.652	-2.1	0.344	0.306	-11.0	1.151	1.183	2.8	0.613	0.688	12.2
6/14	ND-T	ND-T	1000	0.676	0.665	-1.6	0.643	0.549	-14.6	0.592	0.568	-4.0	0.371	0.357	-3.8	1.081	1.031	-4.6	0.565	0.605	7.1
6/15	ND-T	ND-T	250	0.726	0.783	7.8	0.591	0.603	2.0	0.666	0.676	1.5	0.344	0.306	-11.0	1.151	1.165	1.2	0.613	0.672	9.6
6/19	ND-TC	ST-T	c	0.476	0.363	-23.7	0.300	0.274	-8.7	0.510	0.539	5.7	0.210	0.186	-11.4	1.066	0.902	-15.4	0.547	0.493	9.9
6/19	ND-TC	ST-T	400[d]	0.476	0.356	-25.2	0.477	0.459	-3.8	0.509	0.521	2.4	0.348	0.338	-2.9	1.018	0.979	-3.8	0.604	0.509	-15.7
6/20	ND-TC	ND-T	100	0.421	0.409	-2.8	0.345	0.307	-11.0	0.480	0.485	1.0	0.246	0.231	-6.1	1.126	1.121	-0.4	0.620	0.650	4.8
6/21	ND-TC	ND-TC	e	0.476	0.472	-0.8	0.254	0.225	-11.4	0.541	0.464	-14.2	0.173	0.163	-5.8	1.006	1.024	1.8	0.474	0.448	-5.5
6/22	ND-TC	ND-T	100	0.421	0.286	-32.1	0.345	0.324	-7.0	0.480	0.470	-2.1	0.246	0.227	-7.7	1.126	1.091	-3.1	0.620	0.636	2.6
6/26	ND-TC	ND-TC	100	0.421	0.441	4.8	0.345	0.365	5.8	0.480	0.543	13.1	0.246	0.266	8.1	1.126	0.187	5.4	0.620	0.666	7.4
6/27	ND-TC	ND-T	250	0.476	0.474	-0.4	0.477	0.418	-12.4	0.509	0.502	-1.4	0.348	0.331	-4.9	1.018	1.028	1.0	0.604	0.597	-1.2

[a] The nominal value of the daily checkout was ~250 ng. Because a similar point was not used in the initial calibration curve, an approximate response factor was determined by averaging initial response factors at nominal values of 100 and 500 ng.

[b] Vinyl chloride data was not valid because of bad gas standard injection.

[c] The nominal values of the daily check points were 400 ng for vinyl chloride (VC) and 30 ng for all others. Because similar points were not used in the initial calibration curves, the initial response factor used for VC was the highest initial point (250 Ng), and for all others the averages of initial response factors at 20 and 100 ng were used.

[d] The nominal value of the daily check point was ~400 ng. Because a similar point was not used in the initial calibration curve, the response factor at the highest initial point (250 ng) was used.

[e] 250 ng for VC; 20 ng for all others.

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the daily checks. Both tables are similar from that point on. The level of the calibration point used to make the daily check is presented in nanograms. Except as noted, approximately the same level applied to all the targets. The response factors obtained for that level during the initial weekly calibration and the daily check are shown for each compound. The percentage difference in the response factors for each daily check and the initial curve is also shown; a positive percentage indicates that a sample equal to the check-point standard amount (e.g., 250) analyzed on that day would be quantitated as a higher amount if the quantitation were based on the initial calibration data. Because the daily check point was used to generate a revised curve, however, the bias would neither be as great as that indicated, nor would it be eliminated.

The dates listed in Tables C-5 and C-6 are for the daily checks; the dates the initial curves were generated are not shown. In Table C-5, the daily checks between 4/23 and 4/26 are referenced to ST-T and ND-T calibration curves generated on 4/20. Data on 5/1 and 5/2 are referenced to the initial ND-T curve on 4/30. The daily check data between 5/8 and 5/11 are compared with both an ND-T curve and single-point ST-T calibration references on 5/7. The daily check on 5/15 was referenced to the ST-T curve on 5/14, the checks between 5/22 and 5/25 were referenced to the ND-T curve on 5/21, and so on. In Table C-6 the ST-TC daily check on 4/24 was referenced to the curve generated on 4/23, the check on 5/2 to the curve on 5/1, the check between 5/8 and 5/11 to the curve on 5/7, and so on.

The high degree of variation shown by the VC in both tables may be related to its reactivity, as most of the large differences shown are negative. Because the standards were essentially fresh each time, the negative differences were not due to degradation of the standard. Also, the variation

TABLE C-6. SUMMARY OF GC/MS DAILY RESPONSE FACTOR CHECKS FOR ST-TC TRAP CALIBRATION CURVE

Date (1984)	Nominal calib. pt., ng	Vinyl chloride Response factor Initial	Vinyl chloride Response factor Daily check	Vinyl chloride % Difference	Trichlorofluoromethane Response factor Initial	Trichlorofluoromethane Response factor Daily check	Trichlorofluoromethane % Difference	Chloroform Response factor Initial	Chloroform Response factor Daily check	Chloroform % Difference	Carbon tetrachloride Response factor Initial	Carbon tetrachloride Response factor Daily check	Carbon tetrachloride % Difference	Benzene Response factor Initial	Benzene Response factor Daily check	Benzene % Difference	Tetrachloroethylene Response factor Initial	Tetrachloroethylene Response factor Daily check	Tetrachloroethylene % Difference
4/24	250[a]	0.812	0.493	-39.3	0.268	0.253	-5.6	0.574	0.700	22.0	0.310	0.379	22.2	1.096	1.010	-7.8	0.464	0.633	36.4
5/2	250	1.345	0.792	-45.8	0.190	0.155	-18.4	0.513	0.545	6.2	0.186	0.189	1.6	1.058	1.098	3.8	0.567	0.574	1.2
5/8	1200	1.094	0.761	-30.4	0.154	0.126	-18.2	0.470	0.468	-0.4	0.220	0.205	-6.8	0.985	1.020	3.6	0.464	0.487	5.0
5/9	1200	1.094	1.143	4.5	0.154	0.227	47.4	0.470	0.500	6.4	0.220	0.245	11.4	0.985	1.015	3.0	0.464	0.481	3.7
5/10	1200	1.094	0.790	-27.8	0.154	0.179	16.2	0.470	0.502	6.8	0.220	0.239	8.6	0.985	1.017	3.2	0.464	0.485	4.5
5/11	1200	1.094	0.677	-38.1	0.154	0.140	-9.1	0.470	0.463	-1.4	0.220	0.223	1.4	0.985	0.967	-1.8	0.464	0.585	26.1
5/16	100	0.826	0.712	-13.8	0.086	0.096	11.6	0.387	0.419	8.3	0.125	0.144	15.2	1.105	1.183	7.0	0.576	0.615	6.8
5/22	1200	1.013	0.892	-11.9	0.296	0.305	3.0	0.500	0.505	1.0	0.228	0.231	1.3	0.999	1.013	1.4	0.464	0.469	1.1
5/23	1200	1.013	1.011	-0.2	0.296	0.350	18.2	0.500	0.554	10.8	0.228	0.249	9.2	0.999	1.073	7.4	0.464	0.533	14.9
5/24	1200	1.013	0.890	-12.1	0.296	0.300	1.4	0.500	0.508	1.6	0.228	0.253	11.0	0.999	1.015	1.6	0.464	0.482	3.9
5/30	100	0.753	0.475	-36.9	0.305	0.258	-15.4	0.463	0.410	-11.4	0.189	0.167	-11.6	1.196	1.084	-9.4	0.416	0.382	-8.2
5/31	100	0.753	0.451	-40.1	0.305	0.294	-3.6	0.463	0.458	-1.1	0.189	0.188	-0.5	1.196	1.077	-9.9	0.416	0.475	14.2
6/1	100	0.753	0.427	-43.3	0.305	0.246	-19.3	0.463	0.472	1.9	0.189	0.193	2.1	1.196	1.063	-11.1	0.416	0.432	3.8
6/5	100	0.675	0.473	-29.9	0.314	0.283	-9.9	0.530	0.495	-6.6	0.227	0.225	-0.9	0.985	1.021	3.6	0.483	0.435	-9.9
6/5	100	-	b	-	0.314	0.337	7.3	0.530	0.503	-5.1	0.227	0.220	-3.1	0.985	0.920	-6.6	0.483	0.441	-8.7
6/6	100	0.675	0.472	-30.1	0.314	0.272	-13.4	0.530	0.482	-9.0	0.227	0.222	-2.2	0.985	0.915	-7.1	0.483	0.433	-10.4
6/7	100	0.675	0.498	-26.2	0.314	0.301	-4.1	0.530	0.517	2.4	0.227	0.245	7.9	0.985	1.060	7.6	0.483	0.475	-1.6
6/8	20	0.834	0.408	-51.1	0.303	0.245	-19.1	0.572	0.597	4.4	0.184	0.183	-0.5	0.996	1.042	4.6	0.430	0.411	-4.4
6/12	1000	0.918	0.818	-10.9	0.406	0.354	-12.8	0.669	0.629	-6.0	0.351	0.361	2.8	1.077	1.083	0.6	0.604	0.581	-3.8
6/12	2500	-	b	-	0.243	0.316	30.0	0.532	0.566	6.4	0.267	0.313	17.2	0.977	1.009	3.3	0.505	0.531	5.1
6/13	2500	0.597	0.905	51.6	0.243	0.314	29.2	0.532	0.531	-0.2	0.267	0.295	10.5	0.977	0.953	-2.4	0.505	0.534	5.7
6/14	250	0.535	0.398	-25.6	0.360	0.320	-11.1	0.533	0.501	-6.0	0.255	0.250	-2.0	1.259	1.210	-3.9	0.498	0.493	-1.0
6/15	1000	0.918	0.761	-17.1	0.406	0.453	11.6	0.669	0.601	-10.2	0.351	0.342	-2.6	1.077	1.077	0.0	0.604	0.636	5.3
6/19	100	0.394	0.413	4.8	0.208	0.217	4.3	0.393	0.419	6.6	0.192	0.194	1.0	0.903	0.945	4.6	0.468	0.486	3.8
6/20	250	0.353	0.400	13.3	0.251	0.224	-10.8	0.502	0.481	-4.2	0.241	0.228	-5.4	1.165	1.065	-8.6	0.646	0.640	-0.9
6/21	20	0.411	0.278	-32.4	0.189	0.164	-14.3	0.469	0.424	-9.6	0.160	0.152	-5.0	0.957	0.936	-2.2	0.406	0.423	4.2
6/22	100	0.394	0.344	-12.7	0.208	0.203	-2.4	0.393	0.417	6.2	0.192	0.197	2.6	-	c	-	0.468	0.466	-0.4
6/22	100	0.394	0.361	-8.4	0.208	0.199	-1.9	0.393	0.402	2.3	0.192	0.201	4.7	0.903	1.122	24.2	0.468	0.491	4.9
6/28	250	0.353	0.443	25.5	0.251	0.265	2.9	0.502	0.571	13.7	0.241	0.240	-0.4	1.165	1.171	0.5	0.646	0.664	2.8

[a] The nominal value of the daily check point was 250 ng. Because a similar point was not used in the initial calibration curve, an approximate response factor was determined by averaging initial response factors at nominal values of 100 and 500 ng.

[b] Vinyl chloride data were not valid because of bad gas standard injection.

[c] Data for benzene were considered invalid, and the run was repeated.

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in VC in Table C-5 does not appear to be related to trap type; i.e., the ND-TC data are not always worse than those for the Tenax traps, nor are the ST-T data always worse than those for the ND traps.

Closer examination of the data in Table C-5 (other than VC) indicates that the larger values of percentage difference (plus or minus) occurred when the daily check trap was of a different type than the one used to generate the initial curve. Also, there is a trend among trap types for the larger difference values. The ND traps generally yielded a greater response in comparison with the ST-T traps. This pattern was not always true, but generally held in cases of the larger differences (approximately ±20%). The difference in response could be because the ND traps had a better desorption efficiency (or less system loss) than the ST traps.

Examination of the ST-TC trap data in Table C-6 indicates that the highest frequency of relatively large percentage differences occurred for VC and TCFM, the most volatile compounds. Part of the difference could be related to diffusion of these compounds to the charcoal section and subsequent incomplete desorption (as described previously in Section 3). Another reason may be related to the different internal standard (HFB) used for these two compounds. An internal standard more comparable in volatility to VC and TCFM probably should be used.

Evaluation of the data in Table C-5 also suggests that the protocol criterion calling for a limit of ±25 percent difference between initial and daily check response factors should be changed. The criterion in Method 624, which is similar except for the sorbent trap desorption, sets a limit of ±10 percent between the initial calibration and daily checks. The VOST protocol criterion should be changed to ±15 percent, except for vinyl chloride, which should be ±20 percent. The following data analysis justifies these limits.

Daily checks were made on a total of 31 different days for each target compound (30 for VC); however, because more than one check was made on several days, the total number of daily checks was 39 (37 for VC). As previously noted, the initial curves and daily checks were varied between the ND-T, ND-TC, and ST-T trap types, which had yielded similar response factors during preliminary calibration comparisons. On 5 of the 30 days on which daily checks were made for VC, the checks indicated a difference of greater than 20 percent between response factors and the initial weekly curve. Two of these differences, however, could be attributed to comparisons between ST and ND trap types, thus only 3 of 30 checks (10%) between similar trap types (i.e., ST-T and ST-T, or ND and ND) showed differences of more than 20 percent. The comparison between similar trap types is an important consideration because that is the way typical analyses will be conducted; i.e., few (if any) laboratories will be analyzing ND and ST type VOST samples at the same time as done during this study. In the determination of the number of days yielding differences over a specified amount (e.g., 20% for VC), days on which more than one daily check was made were counted as follows: if any checks on a given day differed less than the specified amount, the difference for that day was considered to be less than the amount even if other checks that day indicated a difference greater than the specified amount. Comparisons were made on a compound-by-compound basis. For TCFM, the difference was greater than 15 percent on only 2 of 31 days, and for only 1 of 31 days (3%) when the comparison was between similar trap types. For chloroform, no differences were greater than 15 percent on any of the 31 days. For carbon tetrachloride, differences greater than 15 percent were found on 2 of 31 days, but on only 1 of the 31 days (3%) was the comparison between similar trap types.

For benzene a difference of greater than 15 percent was observed on 1 of 31 days, but it did not represent a comparison between similar trap types. Although the data for tetrachloroethylene indicated that the differences were greater than 15 percent on 5 of 31 days, none of these differences represented comparisons between similar trap types. These data support a change in the protocol criteria limits. Except for VC and TCFM, the data for ST-TC traps in Table C-5 generally support these results. The discussion of results in Section 4 will show, however, that ST traps are not really suitable for these compounds anyway.

Example Data Printouts

The results of each calibration analysis were entered into a library response list as they became available. The computer software calculated the response factor for each calibration point as previously described. Figure C-1 is an example response list for the ND-T, ND-TC, and ST-T calibration data for carbon tetrachloride between 6/11/84 and 6/15/84. The dates listed in the left-hand column are off by one day because of a glitch in the software. Data shown (from left to right) include the area responses of the characteristic ions of the target compound and internal standard, the amounts (in nanograms) of target and internal standards loaded onto the trap, and the response factor. For reference, the trap type used for each calibration is shown in the far right column. The computer software used the first three lines of data to generate and plot the initial calibration curve of A_sC_{is}/A_{is} versus C_s as shown in Figure C-2. The least-squares quadratic-fit curve is plotted through the data points marked by "X". The rest of the response list data in Figure C-1 represent the daily check points. The computer generated a new curve each day. Figure C-3 shows the best-fit curve and data points at

```
RESPONSE LIST, INPUT FILE: VV00005.RL; OUTPUT FILE: VV00005.RL

COMPOUND: CARBON TETRACHLORIDE (Q 117)
REF COMP (VV:    8): D6-BENZENE (IS Q-84)
QUANTITATION MASS:   117   QUANT. MASS (REF.COMP.):      84
                                                                          TRAP
 NO.     DATE* TIME        AREA      AREA(R)        AMNT     AMNT(R)    RESP  TYPE
                                                (NG OC)     (NG OC)
  1  6/12/84 13:14       60847.      631290.     254.300     908.499   0.344  ND-T
  2  6/12/84 14:26      244990.      589567.    1017.000     908.499   0.371  ND-T
  3  6/12/84 15:45      588496.      586691.    2542.400     908.499   0.358  ND-T
  4  6/13/84 10:36      241776.      544848.    1017.000     908.499   0.396  ND-TC
  5  6/13/84 13:06      518559.      479810.    2542.400     908.499   0.386  ST-T
  6  6/14/84 12:03      174883.      163811.    2542.400     908.499   0.381  ST-T
  7  6/14/84 14:55      178215.      182668.    2542.400     908.499   0.349  ND-T
  8  6/14/84 17:43       17284.      201803.     254.300     908.499   0.306  ND-TC
  9  6/15/84 12:38      203458.      509290.    1017.000     908.499   0.357  ND-T
 10  6/16/84 10:28       44918.      523701.     254.300     908.499   0.306  ND-T

   *ACTUAL DATES ARE INDICATED DATES MINUS ONE DAY.
```

Figure C-1. Example response list for ND-T, ND-TC, and ST-T calibration data for carbon tetrachloride.

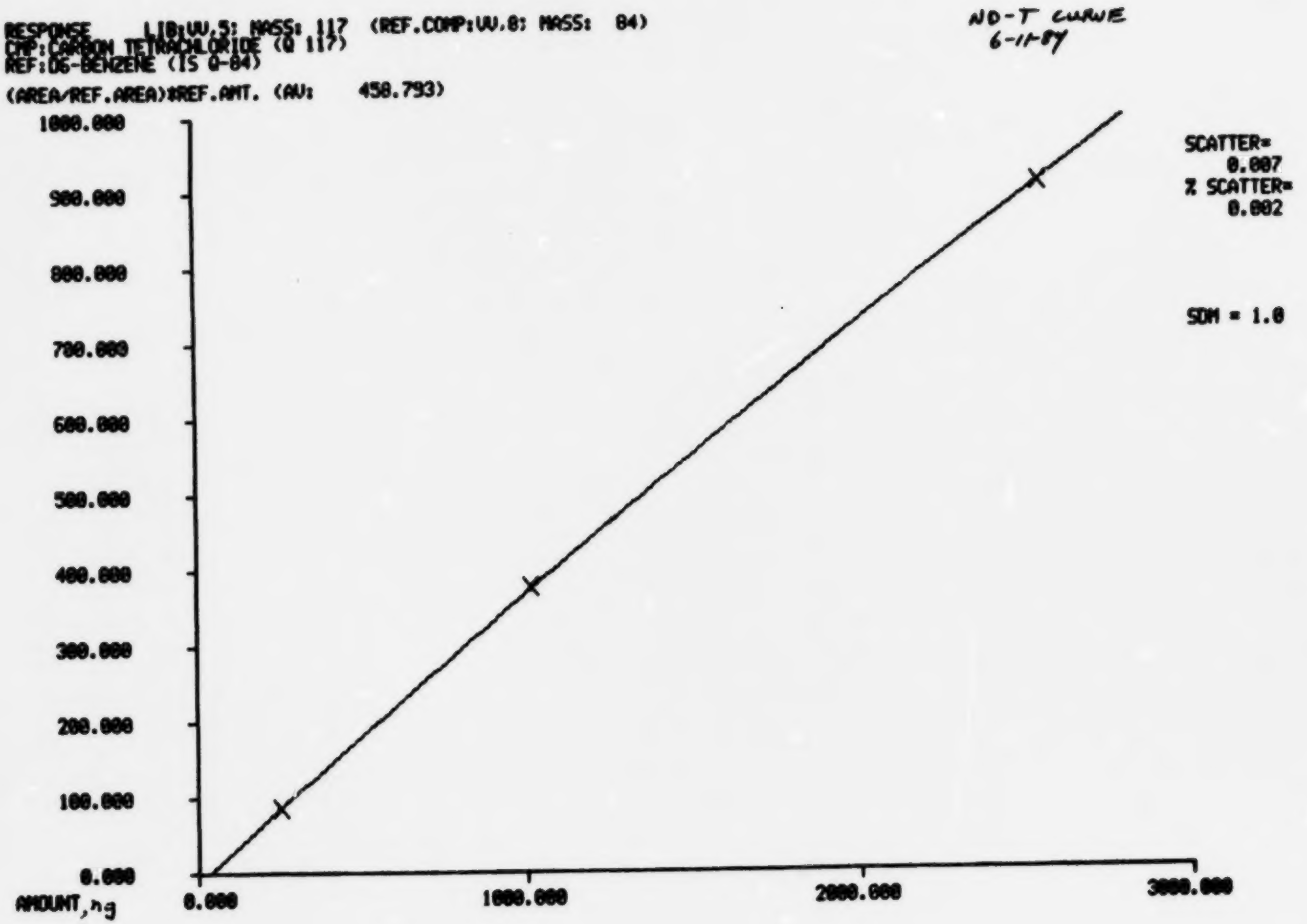

Figure C-2. Example of initial weekly calibration curve for carbon tetrachloride.

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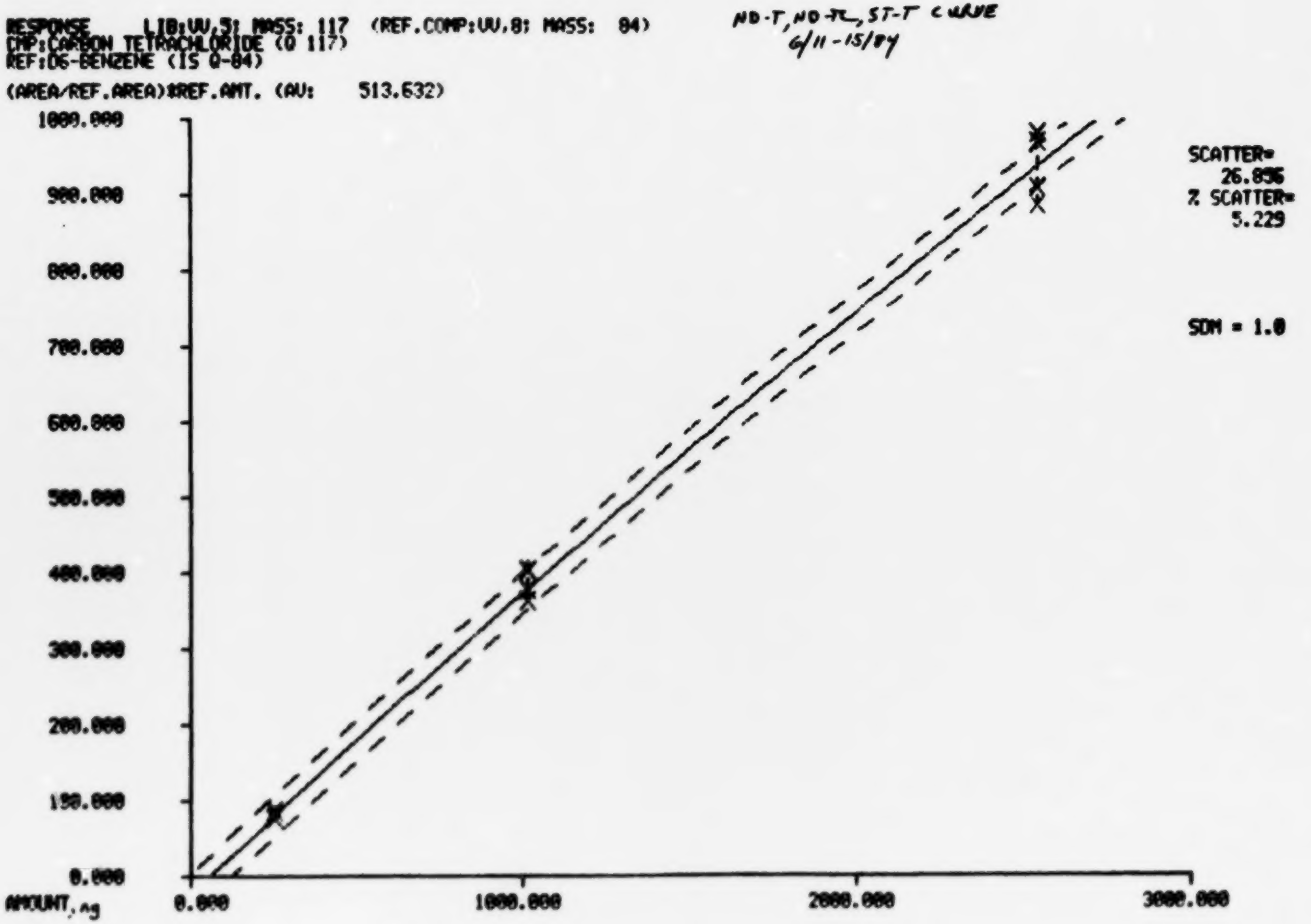

Figure C-3. Example of calibration curve for carbon tetrachloride including daily check points.

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the end of the week. The dashed lines on either side of the curve represent the amount of scatter in the data.

We used the curve of A_sC_{is}/A_{is} versus C_s to depict instrument response rather than the plot of RF versus area that was actually used in the quantitation because the RF plot is not as easy to interpret. For example, Figure C-4 shows the RF versus A_s curve for the response list in Figure C-1 and reflects the same instrument behavior as just shown in Figure C-3. Clearly, the plot of A_sC_{is}/A_{is} versus C_s (Figure C-3) is more indicative of instrument response than Figure C-4. The difference in scales of the y-axis can be misleading, however, because the apparent high degree of variation in Figure C-4 represents a "scatter" of 3.7 percent compared with 5.2 percent in Figure C-3. It should be pointed out that the curve of A_sC_{is}/A_{is} versus C_s cannot be used internally by the computer software to quantitate results even though the computer will plot it. It may be beneficial to quantitate results externally from the computer using the curve more indicative of response.

GC/MS SYSTEM AND ANALYSIS BLANKS

An analytical system blank (a complete desorption and analysis cycle without a sorbent trap in the desorber) was run several times during the laboratory study to ensure that the system was free of interferences. For these runs, the internal standards were injected into the purge vessel. Table C-7 summarizes the system blank data for the six target compounds. In all cases the system had less than 3.5 ng of any target. The first system blank on 6/27 followed an ST-TC calibration point, and the indicated blank values are probably due to residual in the system. The repeat blank showed a clean system.

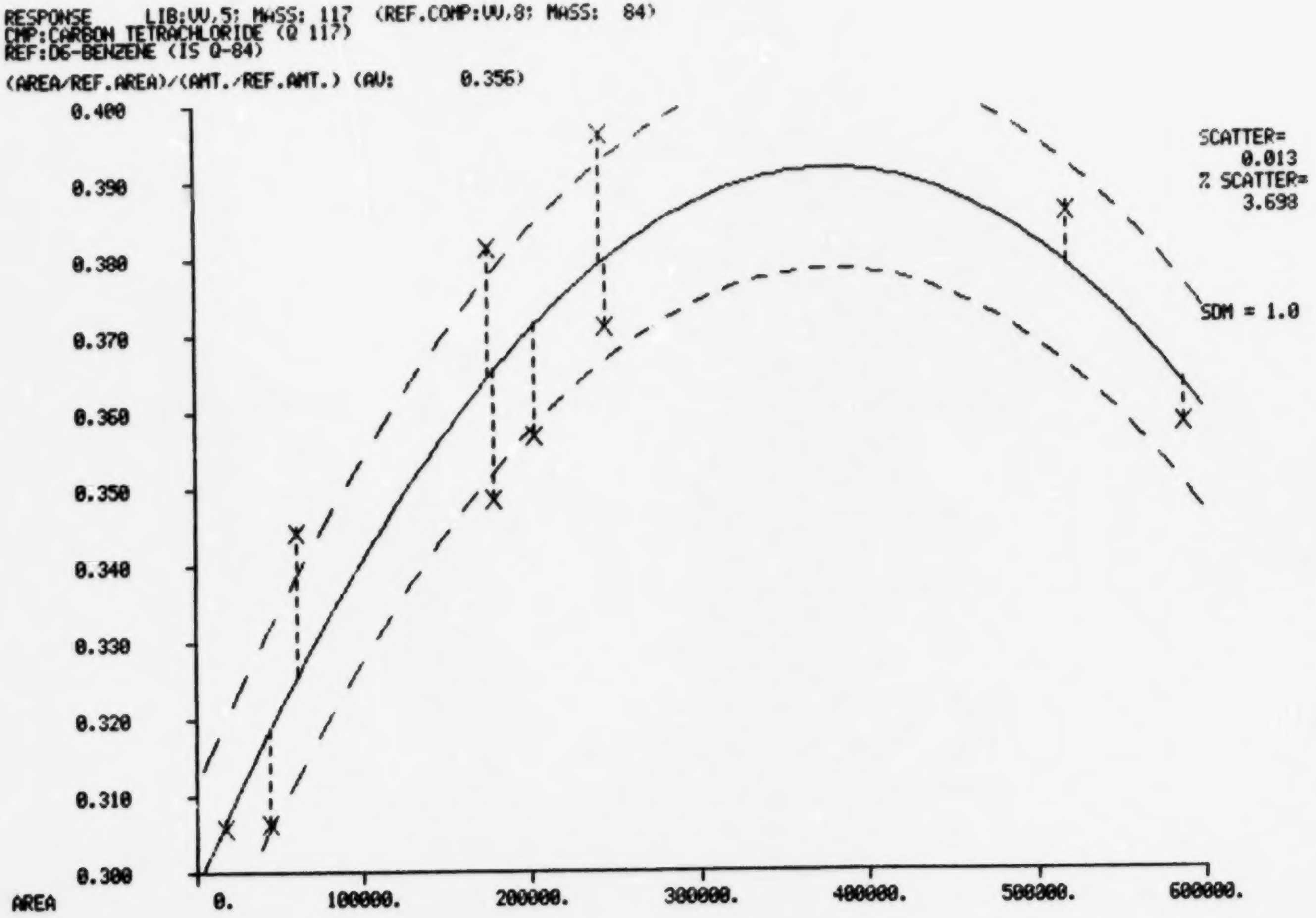

Figure C-4. Example of RF versus area calibration curve for carbon tetrachloride.

TABLE C-7. GC/MS ANALYTICAL SYSTEM BLANK DATA (ng)

Date (1984)	Type of trap thermal desorber system[a]	Compound					
		VC	TCFM	$CHCl_3$	CCl_4	Benzene	PERC
4/25	ND	-[b]	-	-	-	0.8	0.6
4/25	ST	-	-	-	-	0.9	-
4/25	ST	-	-	-	-	3.3	-
4/25	ST	-	-	0.2	-	1.3	-
5/3	ST	-	-	-	-	1.0	-
5/8	ST	-	-	-	-	2.5	-
6/6	ST	-	-	2.9	-	2.5	2.3
6/27	ST	5.7	-	4.5	0.2	2.6	1.2
6/27	ST	-	-	-	-	1.5	-

[a] Except for trap desorber oven, all other system components are common.

[b] A dash (-) means none of the compound was detected.

On each day of analysis an analytical blank was run, as specified in the protocol, to demonstrate freedom from interferences. This analytical blank (made following the daily GC/MS performance test) involved desorption and analysis of a sorbent trap, which generally was then used in the GC/MS calibration. The type of trap used in the analytical blank was varied among all four types. The tight analytical schedule usually did not permit more than one analytical blank per day. Results are shown in Table C-8. These blank levels were generally higher than the system blanks. Almost all of the higher values were related to the ST-TC traps. Because these traps were used repeatedly in instrument calibration during the laboratory study, the occasional appearance of high blank values may have been related to incomplete desorption efficiency, as previously described. When high blank values were detected, the trap was replaced or was baked out overnight in the appropriate desorber oven.

The protocol specifies that an analysis blank should be run at the beginning of each day. An addition should be made requiring that an acceptable system blank be run prior to analysis of blank samples, especially if the blank follows a high-level sample analysis. A system blank should also be run when going from a high-level to a low-level sample. This procedure would ensure against any residual in the analytical system biasing the results of subsequent analyses. For example, if 1 percent of an analysis typically remains in the system as residual, a blank trap run immediately after a 1000-ng sample or standard would be biased high by 10 ng. This level of residual would not have any significant effect on the samples, but it could make blanks seem worse than they really were.

The blank levels were reported as being the target compound as long as the primary characteristic ion was present at its expected retention times.

TABLE C-8. GC/MS ANALYSIS BLANK DATA[a]
(ng)

Date (1984)	Trap type	Compound					
		VC	TCFM	$CHCl_3$	CCl_4	Benzene	PERC
4/24	ND-TC	-	-	0.4	-	5.8	-
4/30	ND-T	-	-	0.6	-	2.2	1.7
5/1	ST-TC	5.0	-	0.2	-	4.8	0.2
5/2	ND-TC	-	-	0.1	1.5	1.7	0.6
5/3	ST-T	-	-	0.5	-	2.3	4.8
5/7	ST-TC	-	-	-	-	1.3	-
5/7	ND-T	-	-	-	-	1.9	-
5/8	ND-TC	-	-	-	-	4.0	-
5/9	ST-T	-	-	-	-	3.9	16.9
5/10	ST-TC	54.3	-	4.6	-	7.2	-
5/11	ND-T	-	-	-	-	0.6	-
5/14	ST-T	-	-	2.5	0.4	4.9	39.3
5/14	ST-TC	9.2	48.2	7.8	-	7.4	5.3
5/15	ND-TC	-	-	2.0	-	3.1	1.4
5/21	ND-T	-	-	-	-	1.6	-
5/21	ST-TC	-	-	-	-	4.4	-
5/22	ND-TC	-	-	0.8	-	3.5	-
5/23	ST-T	-	-	-	-	2.1	1.8

(continued)

TABLE C-8 (continued)

Date (1984)	Trap type	Compound					
		VC	TCFM	$CHCl_3$	CCl_4	Benzene	PERC
5/24	ST-TC	111.6	-	1.9	-	7.5	-
5/25	ND-TC	-	-	1.8	-	5.3	0.2
5/29	ND-TC	-	-	3.5	1.9	2.5	1.7
5/29	ST-TC	120.8	13.4	9.5	-	22.7	7.0
5/30	ND-T	-	0.1	3.8	-	3.3	3.1
5/31	ST-T	-	0.5	4.8	4.3	5.1	30.6
5/31	ST-T	0.9	0.3	3.9	0.2	3.2	5.2
6/1	ST-TC	9.0	0.2	5.5	-	5.9	5.5
6/1	ST-TC	2.5	0.2	4.1	1.0	4.9	6.3
6/4	ST-T	0.1	1.0	5.5	-	2.5	2.4
6/4	ST-TC	5.6	0.3	4.9	-	6.0	3.7
6/5	ND-T	-	-	3.7	-	4.4	2.1
6/6	ST-TC	8.0	0.5	4.3	-	5.3	3.9
6/7	ND-TC	-	-	4.2	-	3.0	2.0
6/8	ST-TC	3.4	-	5.0	-	9.0	3.1
6/8	ST-TC	1.3	-	6.0	-	7.8	6.1
6/11	ST-TC	1.8	-	4.2	-	11.0	4.2
6/11	ND-T	-	-	2.7	-	9.4	0.4
6/12	ND-TC	-	-	3.2	-	6.3	1.1
6/13	ST-T	-	-	3.0	-	5.5	1.2
6/14	ST-TC	13.5	-	10.2	-	7.8	3.4

(continued)

TABLE C-8 (continued)

Date (1984)	Trap type	Compound					
		VC	TCFM	$CHCl_3$	CCl_4	Benzene	PERC
6/15	ND-T	-	-	3.5	-	5.1	1.8
6/18	ST-TC	23.2	-	4.0	-	3.6	8.0
6/18	ND-TC	0.3	-	2.0	-	4.4	1.9
6/19	ST-T	-	0.2	5.2	1.5	8.0	51.5
6/19	ST-T	1.8	-	4.0	-	4.4	3.3
6/20	ND-T	-	-	4.0	-	10.4	1.8
6/21	ST-TC	18.4	-	5.1	-	7.4	2.7
6/22	ND-T	1.1	-	3.7	-	12.1	1.5
6/26	ND-T	-	-	4.3	-	2.8	1.3
6/27	ND-T	-	-	5.4	-	9.5	1.3

[a] Analysis blank includes entire system plus a VOST trap that was used for loading calibration standards.

[b] A dash (-) means none of the compound was detected.

This does not mean that a positive identification of the target compound was made. The nanogram levels present in some of the blanks were simply too low to produce enough mass spectral information to confirm the identity of the compound. Results were reported as the target compound anyway because the effect on sample analysis (bias to results) would be the same regardless of the origin of the principal ion.

GC/MS DATA REDUCTION AND VALIDATION

This subsection discusses the procedures used to identify and quantitate the target compounds in samples and blanks.

Qualitative Identification

As previously described, each sample analysis consisted of a reconstructed ion chromatogram (RIC); a list of calculated areas of each peak on the RIC; an EICP of the principal characteristic ion for each target and internal standard; a quantitation list containing the principal ion area and total nanograms for each target compound present (based on the presence of the principal ion) and the internal standard; and the background-corrected, mass-spectral fragmentation pattern of each target present in the sample.

The computer was also programmed to search the reference library and identify three compounds whose mass spectra best matched the spectra in the sample. The spectra for these three compounds were printed on the same page as each target whose principal ion was detected in the sample at the proper retention time (± 30 seconds). If the computer search identified the list match as the target compound, a positive identification was presumed. For many of the lower-level samples, the first computer match was not the target compound, probably because of the presence of interfering spectra. In these cases, the sample spectra were examined to see if the target compound spectra were contained within the sample spectra at the proper abundance ratios between primary and secondary ions. This was done by visually comparing the calibration spectra and sample spectra. If the target compound ions were present in the sample spectra at the proper ratios, the presence of the target was presumed to be confirmed, even if interferent ions were also present. Very few problems were encountered with interferences with the primary ions of any compound except vinyl chloride and benzene, which each have one large primary ion and very small secondary ions. For these and other compounds that have only one ion in relatively large abundance, positive identification can be practically impossible in the presence of interferences in low-level samples.

In this laboratory study, the expected amount of target compound in a given sample was known, and a qualitative identification was not necessary except for low-level samples and blanks. In real samples, in which the amount of target compound will not be known, qualitative identification near method detection limits may not meet the specified criteria, which are the same as those in Method 624. The VOST protocol has a target detection limit of 2 to 10 ng per sample (or as low as 1 ng if sample traps are analyzed individually). Method 624 detection limits, however, vary from approximately 8 to 36 ng per sample, depending on the target compound. These Method 624 levels are based on the ability to determine, with 99 percent probability, that the measured level is greater than zero. At lower nanogram levels, mass spectra obtained from the sample may not contain enough critically important secondary ions to meet the qualitative identification criteria specified in the protocol (or Method 624). The lack of abundance of strong secondary ions in such spectra may cause library searches to yield meaningless matches (possible identities). Also, at low nanogram levels, background interferences may result in a base mass peak that does not represent the primary ion of the target compound. This complicates identification even more.

The types of identification problems just described were experienced to some extent in the low-level samples and blanks. All of these problems can yield only positive biases to results, as a target compound could be presumed to be present when actually it was not. There is no doubt that the GC/MS analytical system is sensitive enough to detect masses as low as 2 ng; however, if a high degree of probability in positive identification is desired, the VOST protocol detection limits seem unreasonably low. A target detection limit of 50 ng per analysis (single trap or paired traps) is recommended. This level does not take into consideration possible levels of field blanks.

Quantitation of Target Compounds

The amount of analyte in a sample trap was based on the integrated abundance from the EICP of the primary characteristic ion designated for that analyte and its corresponding internal standard. Using the internal standard procedure, the amount of analyte was calculated by the computer software as shown in Equation C-2.

$$\text{Amount of analyte} = A_s C_{is} / A_{is} RF \qquad \text{Eq. C-2.}$$

where A_s = area of the characteristic ion for the analyte to be measured

A_{is} = area for the characteristic ion of the internal standard

C_{is} = amount (ng) of internal standard

RF = response factor calculated from quadratic fit to the calibration curve

The response factor for each target compound was determined internally by the computer software by using the daily updated calibration curve for the appropriate trap type. Results were printed on a quantitation list for each analysis.

APPENDIX D

QUALITY ASSURANCE SUMMARY

QUALITY ASSURANCE SUMMARY

Quality assurance guidelines provide detailed procedures and actions necessary for defining and producing acceptable data. Six such documents were used in this laboratory test program to ensure the collection of acceptable data and to provide a definition of unacceptable data. These documents are 1) the Laboratory Investigation Test Plan prepared by PEI and reviewed by the Quality Assurance Division; 2) the EPA Protocol for the Collection and Analysis of Volatile POHC's Using VOST, February 1984; 3) the EPA Test Method 624-Purgeables, July 1982; 4) the EPA Quality Assurance Handbook Volume III, EPA-600/4-77-027; 5) the PEI Emission Test Quality Assurance Plan; and 6) the PEI Laboratory Quality Assurance Plan. The last two, which are PEI's general guideline manuals, define the Company's standard operating procedures that are followed by the emission testing groups and the laboratory groups.

In this specific test program, the following steps were taken to ensure that the sampling and analytical procedures produced quality data.

1. Calibration of sampling equipment (dry gas meters, rotameters, thermometers, thermocouples).
2. Evaluation of the test gas generation system to verify noncontamination, system integrity, stability, and accuracy.
3. Independent analysis of cylinder test gases to verify labeled values and the stability of gases for the duration of the study.
4. Use of a single lot of Tenax and one lot of charcoal.
5. Initial check of the quality of the lot of Tenax prior to its use, and independent assessment of Tenax quality by two other laboratories.

6. Analytical check of pentane-extracted glass wool for residual pentane prior to its use in packing ND sorbent traps.

7. Documentation of sorbent trap preparation and conditioning activities.

8. Pretest blank check of all sorbent trap pairs by GC/FID, except for one pair per week that was checked by GC/MS.

9. Initial recovery check and system blank check and daily calibration of GC/FID system for blank-checking sorbent traps.

10. Purity checks on target compound calibration materials, except vinyl chloride (VC). The concentration of the VC standard, as an EPA audit material, was traceable to the National Bureau of Standards.

11. Prior to the laboratory study, recovery checks on two analytical traps for use in the Tekmar LSC-2 purge and trap apparatus.

12. Comparison of calibration curves for ND-T, ND-TC, ST-T, and ST-TC trap types.

13. GC/MS tune checks and mass calibration at the beginning of each day of analysis.

14. Three-point calibration of GC/MS analytical system at least weekly for each target compound, and a daily single-point calibration check.

15. GC/MS system blank checks (not including sorbent trap) periodically and analysis blank checks (including blank sorbent trap) daily.

16. Weekly GC/MS system recovery checks by use of on-column injections.

17. Addition of internal standards (IS) for all GC/MS analyses and a weekly plot of IS responses.

18. Separate analysis of sample sorbent traps to allow assessment of breakthrough.

19. Weekly audits by use of EPA cylinder gas audit materials containing unknown concentrations of Group 1 compounds.

20. Analysis of sorbent trap field blanks, trip blanks, and laboratory blanks.

21. Analysis of selected water samples (from the runs in which moisture was added to the test gas) to check for losses or contamination in the sampling system.

22. Collection and analysis of zero-air samples to check for contamination of the quad train.

23. Recovery check of target compounds from spiked sorbent traps after purging with 20 liters of nitrogen.

Table D-1 presents the sampling equipment calibration results. The protocol does not specify any calibration procedures or error limits except that the dry gas meter be accurate to within ± 2 percent. The protocol should include more specific calibration requirements. The dry gas meters and rotameters were calibrated initially over a range of flow rates from 0.25 to 2.0 liters/min. Rotameter calibration curves were generated from the initial data. The post-test calibrations of the dry gas meters were conducted at a flow rate of 1 liter/min. Guidelines in Volume III of the EPA Quality Assurance Handbook for Reference Method 6 were followed.

Subsequently, we discovered that calibration of the dry gas meters against wet test meters (even the small 3-liter-per-revolution size we used) may not be valid at flow rates of less than 1 liter/min because the accuracy of this wet-test meter is only guaranteed down to 1 liter/min by the manufacturer. Therefore, different calibration procedures (for example, measurement of volumes with a bubble meter) should be developed if the dry gas meters are to be used at flow rates lower than 1 liter/min. A possible alternative has been tried but not fully validated.

As described in Section 3, the evaluation of the test gas generation system (Item 2) indicated the device was acceptable.

The cylinder gases used to generate the test gases were analyzed independently by RTI to verify stability of the gases. The cylinder of Group 1 gases was analyzed by RTI before and after the laboratory study, in March and August 1984, respectively. The cylinder of TCFM was analyzed by Scott

TABLE D-1. SAMPLING EQUIPMENT CALIBRATION

Equipment	ID No.	Calibrated against	Expected error	Actual error	Within limits	Comments
Dry gas meter	VOST 1	Wet test meter	$Y_{max}-Y_{min} \leq 0.02\ \bar{Y}_{in}$ $(\bar{Y}_{post\text{-}test}-\bar{Y}_{in}, \leq 0.05\ \bar{Y}_{in})$	0.016 (0.009)	X X	$\bar{Y}_{in} = 1.014$
	VOST 2			0.014 (0.005)	X X	$\bar{Y}_{in} = 1.004$
	VOST 3			0.012 (-0.001)	X X	$\bar{Y}_{in} = 1.002$
	VOST 4			0.017 (0.014)	X X	$\bar{Y}_{in} = 1.014$
Condenser coil thermocouples	QV-1 QV-2 QV-3 QV-4	ASTM-3F	±2°F	+1°F +1°F +1°F +1°F		Maximum deviations
Dry gas thermometer	VOST-1 VOST-2 VOST-3 VOST-4	ASTM-3F	±5°F	+2°F +4°F +2°F +2°F		Maximum deviations

Specialty Gases prior to the study and by RTI after the study, within approximately 1 month of the Group 1 cylinder analysis. Scheduling conflicts precluded an independent analysis of the TCFM cylinder prior to the study. As shown in Table D-2, none of the concentrations measured after the tests differed by more than 10 percent from the values determined prior to the beginning of the VOST laboratory study; therefore, the initial values were considered valid and none of the results were recalculated. The differences (expressed as a percentage) were calculated by subtracting the initial value from the final value and dividing the difference by the initial value.

TABLE D-2. STABILITY OF CYLINDER GASES

Time analyzed	Target compound concentration, ppb					
	VC	TCFM	CF	CT	Benzene	Perc
Before	71.5	89.8	60.6	65.8	66.4	68.4
After	69.8	90.1	64.6	68.2	71.1	69.6
Difference, %	-2.4	+0.3	+6.6	+3.6	+7.1	+1.8

Items 4 through 7 were discussed in Appendix B, Items 8 and 9 in Subsection 3.3, Items 10, 11, 13, 14, and 15 in Appendix C, and Item 12 in Subsection 3.4.

Weekly GC/MS system recovery checks were made by injecting an aliquot of a methanolic calibration standard solution at the head of the GC column and comparing the results with those obtained when the same amount of calibration standard was loaded onto a sorbent trap. The percentage of recovery was determined by comparing the area responses of the primary characteristic ion of each target compound and internal standard (HFB and D_6-benzene) for the sorbent trap analysis with the area responses of the on-column injection. No corrections were made for internal standard recoveries. In this way, any losses of compounds in the desorber oven, purger, analytical trap, connecting fittings, or handling would be determined. We recommend that this type of recovery check be added to the protocol. Table D-3 presents the results obtained during the laboratory study.

Vinyl chloride recoveries were not determined because the relatively large volume of calibration gas required (~3 ml of the 30.6-ppm gas cylinder standard) apparently created too much of a pressure change in the carrier gas flow when injected at the head of the column, which caused erratic results. The successful preliminary trap recoveries (previously described in Appendix C) were made by using a 1028-ppm gas standard of VC, but the tight analysis schedule did not permit us to conduct a separate weekly recovery checks for VC. Therefore, VC was not included when it was determined that the 30.6-ppm standard could not be used effectively in the recovery check.

As shown in Table D-3, these recovery checks helped to correct a problem with the six-port switching valve inside the purge and trap unit. After the valve was repaired on 4/27/84, the recoveries of most compounds improved dramatically. Only preliminary analyses were conducted prior to 4/30/84. The recovery checks on 4/27, 5/1, and 6/4 were the only ones after 4/27 based on ST-T traps; all of the other subsequent checks were based on ND traps. Thus, the low recoveries for perc on these three days and all recoveries on 6/4 may be related to the ST desorption system. The low recoveries on 6/11 may in fact have been caused by a small leak somewhere in the analytical system. It should be noted that the low recoveries for TCFM on 5/1, 6/4, 6/11, and 6/13 and all recoveries on 6/4 would be improved considerably after adjustment for

TABLE D-3. GC/MS SYSTEM RECOVERY CHECK DATA[a]
(Percent recovery of on-column injection area)

Date (1984)	Compound						
	HFB	TCFM	$CHCl_3$	CCl_4	Benzene	Perc	D_6-Benzene
4/23	64	76	81	82	72	67	68
4/24	60	77	76	84	70	50	56
4/25	59	97	84	96	67	65	62
4/26	63	105	84	99	68	63	68
4/27[b]	91	100	101	97	101	78	85
4/30	109	91	106	102	113	106	107
4/30	112	98	112	111	119	104	115
5/1	89	75	92	84	96	72	90
5/8	93	85	95	92	100	94	94
5/21	111	97	108	102	108	103	124
6/4	83	72	78	68	78	64	75
6/11	93	68	74	72	83	82	94
6/13	90	70	91	87	102	83	96
6/18	99	98	96	98	103	99	100

[a] Vinyl chloride (VC) was not included in recovery checks because numerous on-column injections of the separate VC gas standard did not yield reproducible results.

[b] After repair of 6-port valve in Tekmar purge and trap unit.

the internal standard response. Table D-4 summarizes the mean percent recoveries and standard deviations(S)for checks made from 4/27 to 6/18/84.

TABLE D-4. RECOVERY CHECK SUMMARY

	HFB	TCFM	$CHCl_3$	CCl_4	Benzene	Perc	D_6-Benzene
Mean, %	97	85	95	91	100	88	98
S,%	10	13	12	14	12	15	14

Internal standards were included in every analysis to track GC/MS performance. Approximately 250 ng of each IS was added during weeks when the instrument was set for analysis of the low-level samples, and approximately 1000 ng was added during weeks when the high-level samples were analyzed. The same amount of IS was always added at given instrument sensitivity settings to permit direct comparison of area responses for that sensitivity.

Table D-5 presents the internal response data on a daily basis. All of the data of the low-level sensitivity setting are presented first. Data for the ST-TC traps are shown separately because of the difference in absolute response obtained for this type of trap (as previously discussed in Section 3). The mean area response and percent relative standard deviation are shown for each IS for all analyses conducted each day.

Figure D-1 is a graphical representation of the area response data for HFB from May 7 through May 11, 1984, for analyses related to ND-T, ND-TC, and ST-T trap types. Each "X" in the figure represents the HFB response for an individual analysis. The solid horizontal line through the data represents the average area response for the entire week, and the dashed lines above and below the solid line represent plus and minus one standard deviation. The IS plots can be useful for pointing out suspect analyses, as evidenced by the

TABLE D-5. GC/MS INTERNAL STANDARD RESPONSE DATA

	(ST-T, ND-T, and ND-TC Traps)				(ST-TC Traps)			
	d_6-Benzene		HFB		d_6-Benzene		HFB	
Date (1984)	Area, 1000 units	RSD,[a] %	Area, 1000 units	RSD, %	Area, 1000 units	RSD, %	Area, 1000 units	RSD, %
4/23[b]	391	23.2	326	24.6	168	47.8	110	45.0
4/24[b]	322	6.6	263	4.9	117	4.4	97	2.9
4/25[b]	403	27.7	310	26.0	N/A[c]	N/A	N/A	N/A
4/26[b]	413	36.1	347	30.2	N/A	N/A	N/A	N/A
4/27[b]	490	10.9	380	9.4	N/A	N/A	N/A	N/A
4/30[b]	505	5.7	361	6.6	N/A	N/A	N/A	N/A
5/1[b]	409	8.5	302	8.7	158	3.1	102	8.7
5/2[b]	399	8.8	284	6.5	154	2.3	116	1.5
5/3[b]	356	11.9	268	4.9	N/A	N/A	N/A	N/A
5/14[b]	329	6.8	353	4.0	161	14.3	159	13.1
5/15[b]	364	8.9	369	3.6	177	3.8	177	5.4
5/16[b]	363	10.2	309	6.4	156	N/A	127	N/A
5/17[b]	376	14.6	296	8.8	N/A	N/A	N/A	N/A
5/18[b]	328	6.6	284	9.1	175	4.7	146	3.8
5/29[b]	278	10.2	225	8.5	156	4.2	131	2.9
5/30[b]	262	6.6	213	4.3	132	6.3	113	2.9
5/31[b]	301	4.5	269	6.0	165	10.8	154	22.8
6/1[b]	320	5.3	289	9.3	180	27.1	184	27.9

(continued)

TABLE D-5 (continued)

Date (1984)	(ST-T, ND-T, and ND-TC Traps)				(ST-TC Traps)			
	d_6-Benzene		HFB		d_6-Benzene		HFB	
	Area, 1000 units	RSD,[a] %	Area, 1000 units	RSD, %	Area, 1000 units	RSD, %	Area, 1000 units	RSD, %
6/4[b]	281	7.5	269	11.4	136	5.0	131	6.1
6/5[b]	288	13.9	271	5.2	140	5.5	132	9.4
6/6[b]	253	7.5	259	7.1	132	8.7	134	5.7
6/7[b]	309	11.0	291	10.9	154	13.9	151	12.3
6/8[b]	300	6.2	270	3.4	150	4.5	139	3.7
6/18[b]	246	8.0	245	5.7	131	9.6	138	13.5
6/19[b]	236	7.3	243	6.7	144	9.5	151	11.0
6/20[b]	257	7.9	266	5.6	163	15.9	181	18.6
6/21[b]	198	30.8[d]	204	30.6[d]	82	63.4[d]	91	65.2[d]
6/22[b]	240	11.3	243	7.6	155	28.2	161	27.8
6/26[b]	249	2.2	243	14.4	N/A	N/A	N/A	N/A
6/27[b]	245	9.6	234	11.5	123	25.6	116	32.6
5/3	393	8.0	289	8.0	N/A	N/A	N/A	N/A
5/7	428	9.0	308	7.7	165	8.7	122	2.1
5/8	458	5.2	350	7.0	166	N/A	128	N/A
5/9	442	9.9	333	6.4	205	11.7	140	5.2
5/10	335	33.1	257	32.6	159	13.4	121	11.6
5/11	352	22.7	315	22.6	169	26.7	152	29.4
5/21	420	5.3	291	3.7	197	3.0	143	9.4
5/22	378	5.9	274	4.3	195	2.9	144	11.0

(continued)

TABLE D-5 (continued)

Date (1984)	(ST-T, ND-T, and ND-TC Traps)				(ST-TC Traps)			
	d_6-Benzene		HFB		d_6-Benzene		HFB	
	Area, 1000 units	RSD,[a] %	Area, 1000 units	RSD, %	Area, 1000 units	RSD, %	Area, 1000 units	RSD, %
5/23	362	7.0	265	4.2	196	3.2	139	13.1
5/24	389	6.0	266	6.5	195	2.0	138	8.0
5/25	344	14.3	223	5.2	155	0.1	124	0.3
6/11	579	7.2	457	4.3	270	13.2	233	19.5
6/12	530	9.6	461	7.0	241	4.8	200	6.2
6/13[e]	179	9.6	168	5.0	82	N/A	66	N/A
6/14	485	4.1	433	3.0	236	13.1[d]	233	16.0[d]
6/15	488	8.3	424	5.7	283	10.1	265	14.8

[a] Relative standard deviation, percent = standard deviation/mean x 100.

[b] Instrument multiplier voltage set for low-level analysis. All other values are for high-range analysis.

[c] N/A = Not applicable.

[d] RSD values are biased high because of variation in instrument response during the day; i.e., overall response was low for part of the day and normal for the remaining portion.

[e] Overall response was lower than normal throughout the day.

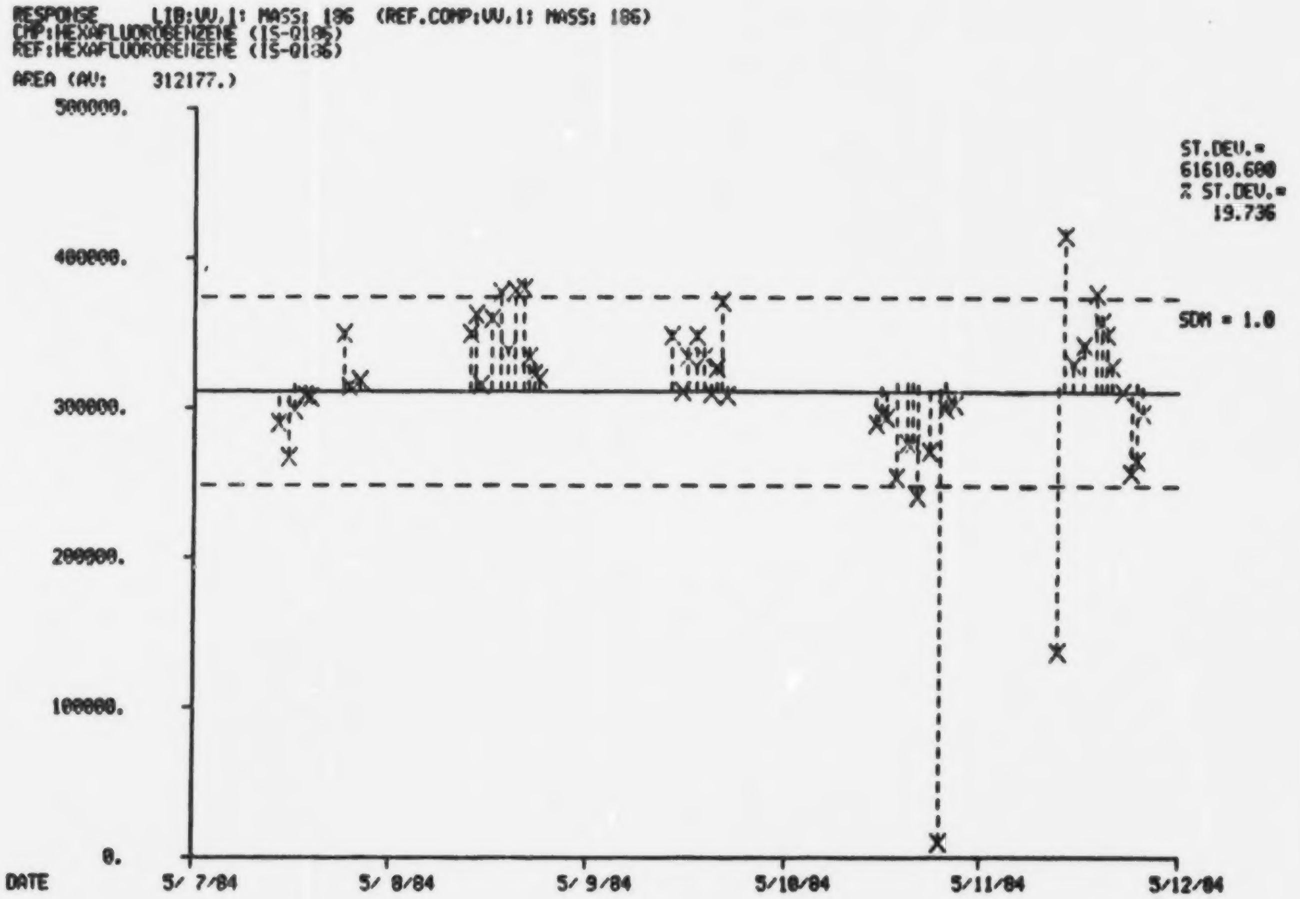

Figure D-1. Plot of HFB area response for ND-T, ND-TC, and ST-T analyses the week of May 7, 1984.

two very low responses, one each on May 10 and 11, 1984. These two analyses, obviously outliers, were the ones previously identified in Section 4 as being improperly loaded with internal standard. The corresponding data for May 10 and 11 in Table D-4 (which indicate an RSD value of 33 and 23 percent respectively for the daily HFB responses) include those outliers. Exclusion of the two outliers reduces the daily RSD values for May 10 and 11 to 7 and 14 percent respectively. These values are more in line with those for the other days that week (8, 7, and 6 percent RSD for HFB on May 7, 8, and 9, respectively).

As shown in Figure D-1, the instrument response for the week of May 10 was relatively stable. The degree of stability shown for this week was not demonstrated every week, as indicated by Figure D-2, a plot of HFB response for the week of April 30, 1984, for the same types of traps (ND-T, ND-TC, and ST-T). Figure D-2 is similar to Figure D-1 except that the solid line represents the best-fit linear curve through the data points instead of a simple average of the data. The slope of the line in Figure D-2 clearly shows the decrease in response over the week compared with the general stability of response shown in Figure D-1. The difference in instrument stabilities shown by the two figures indicates that tracking IS response data over a long term, as suggested in the protocol, may not be as helpful in spotting suspect analyses as tracking the IS responses on a daily or weekly basis.

The Tenax and Tenax/charcoal sorbent traps in a given sample were analyzed separately to assess if breakthrough occurred. Results were presented previously in Section 4.

Audits were conducted at the beginning of all but one analysis week during the laboratory study using cylinder gases containing unknown concentrations of Group 1 compounds. The gas cylinders were supplied by EPA

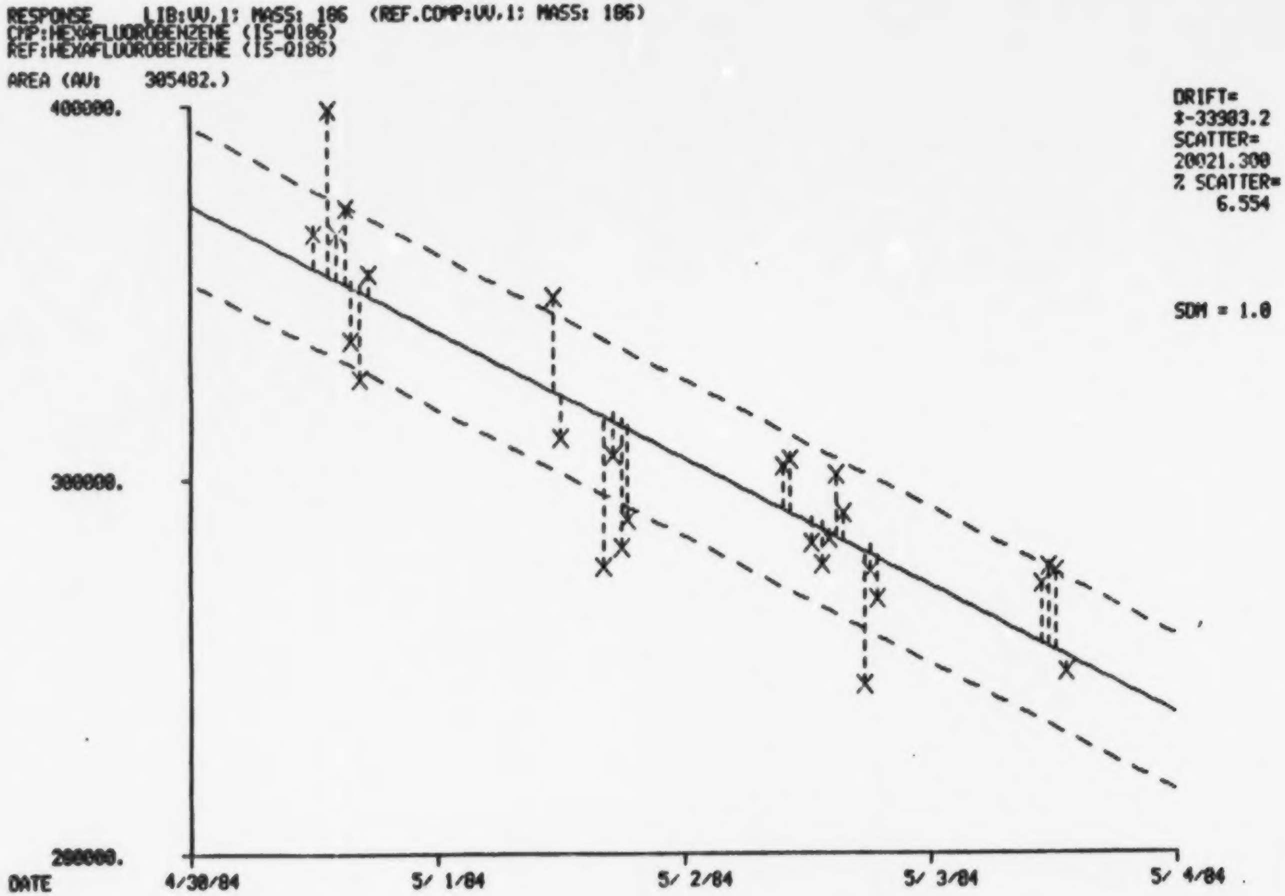

Figure D-2. Plot of HFB area response for ND-T, ND-TC, and ST-T analyses the week of April 30, 1984.

through RTI in conjunction with EPA's gas cylinder audit program. Two types of audits were conducted. The first type, designated as a dilution system audit, was conducted by feeding the audit gas through the dilution system directly onto a pair of ND traps connected in series. The audit gas was not diluted as it passed through the dilution system, but the control valves in the system were used to regulate the flow rate of the audit gas. The actual flow rate of the audit gas was measured with a bubble meter before and after collection of the audit sample. The total audit sample volume was determined by the gas flow rate and the time the sorbent traps were exposed to the audit gas. The second type of audit, designated as a sampling train audit, was conducted by feeding the audit gas through the dilution system (again undiluted) and through the test gas manifold. Two ND sampling trains were used to collect replicate audit samples simultaneously from the manifold, and the excess audit gas was vented.

Each collected audit sample was analyzed as a pair (both the Tenax and Tenax/charcoal traps were analyzed simultaneously) by GC/MS. Results for each Group 1 compound were calculated in parts per billion and reported to the Project Officer, who indicated whether the results were within the acceptable limits (±50 percent of the expected concentration).

The dilution system audits were conducted five times during the laboratory study (on the same cylinder). The sampling train audits were conducted twice (on different cylinders).

A sample volume of 10 liters was specified for all audits, but different volumes were sampled each week, depending on the calibration range being used for the GC/MS that week. The particular volume sampled was estimated to keep the amounts of target compounds on the audit samples within the GC/MS calibration range. Because the audit gas concentrations were unknown (except that they were between 7 and 90 ppb), the estimate of sample volume required to be in the calibration range was at best a rough approximation.

As shown in Table D-6, the audit results were generally acceptable. The ±50 percent accuracy criterion was met for benzene in all cases except for one of the audits that was conducted during a week in which the GC/MS calibration curve was in the low-level range and a small audit sample volume was used. The results were biased high, possibly as a result of sorbent blank levels. The same situation was true for the tetrachloroethylene audit results, but a different sample was involved.

Conversely, audit results for vinyl chloride were unacceptably low for four of the nine separate samples, and they were near the low end of the criterion limit for three of the remaining five audit samples. The audit results for VC supported the general results of the laboratory study that suggest the VOST protocol is ineffective for measurement of VC at the tested conditions.

Precision of the replicate sampling train audits was good. The relative standard deviation values for any pair were less than 12 percent RSD. The precision of all the dilution system audits, which were conducted with the same cylinder, were 36 percent RSD for VC; 9 percent RSD for chloroform; 22 percent RSD for carbon tetrachloride; 14 percent RSD for benzene, excluding the biased sample (or 36 percent RSD if it is included); and 9 percent RSD for tetrachloroethylene.

Analysis of field blanks, trip blanks, and laboratory blanks were discussed in Section 4.

TABLE D-6. SUMMARY OF VOST GAS CYLINDER AUDITS

Date (1984)	Type of audit	Audit gas cylinder No.	Sample volume, liters	Range of amounts detected in sample, ng	Measured concentration, ppb					Results acceptable?[b]
					Vinyl chloride	Chloro-form	Carbon tetra-chloride	Benzene	Tetra-chloro-ethylene	
5/1	Dilution system[a]	BAL 11781	1.4	26-213	7.09	19.1	22.7	25.0	21.3	Yes, but VC low.
5/8	Dilution system	BAL 11781	5.4	192-766	13.6	16.9	17.9	40.4	20.4	All except benzene; value biased by blank level.
5/21	Dilution system	BAL 11781	17.0	273-2200	6.18	15.0	11.7	18.0	18.8	All except VC which was low.
5/29	Dilution system	BAL 11781	1.5	27-183	6.83	18.1	19.0	21.1	17.1	Yes, but VC low.
6/4	Dilution system	BAL 11781	1.5	40-206	10.7	16.8	19.5	20.7	20.6	Yes
6/11	Sampling train[c]	AAL 11888	9.9	84-2360	3.28	48.2	11.2	23.8	11.5	All except VC which was low.
6/11	Sampling train	AAL 11888	9.8	71-2400	2.78	49.5	11.8	23.3	12.2	All except VC which was low.
6/18	Sampling train	AAL 11915	2.0	77-423	15.3	7.97	8.02	37.5	31.4	Yes
6/18	Sampling train	AAL 11915	1.9	66-492	13.1	8.48	8.02	38.8	36.9	All except tetrachloroethylene (high) and VC (low).

[a] Cylinder gas was fed through one port of the dilution system directly onto a pair of sorbent traps connected in series. Sample volumes were determined by product of sampling rate and time.

[b] Current criteria limits are ±50%.

[c] Cylinder gas was routed through one port of the dilution system and through the manifold. Two sampling trains of the quad VOST collected samples simultaneously from the manifold. Excess gas was vented.

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Table D-7 presents a summary of the analyses on water samples taken from the moisture generation apparatus after a test run and on water condensate collected in the primary sample-train flasks (including a water rinse of the first condenser coil). Project schedule and budget constraints precluded analysis of all the samples; however, several representative samples were selected for analysis to check for potential contamination of the sample and for loss of target compounds in the moisture-generation apparatus. No vinyl chloride, TCFM, carbon tetrachloride, or tetrachloroethylene was detected in any of the selected samples except for the water sample from the moisture-generation apparatus for Run RR4. This sample contained a multitude of compounds, probably coming from the Teflon impinger used in the moisture-generation device for this run. One of the many compounds was either TCFM or TCFM plus an interferent, because the sample contained an amount equivalent to approximately 2000 ng of TCFM. As noted in Appendix E, the TCFM results for the VOST samples were greatly biased by this contamination. The overall contamination in the water sample for Run RR4 is shown by the normalized RIC area, which is much higher than in most of the other samples. The amounts of chloroform and benzene detected in the Run RR4 water sample (5.1 and 66.7 ng, respectively) represented approximately 0.6 and 3.0 percent of the total amounts of the respective target compounds detected in the corresponding VOST samples.

Sample No. ST334, the condensate sample for Run W7, contained approximately 14 ng of benzene compared with 35 ng detected in the sample sorbent traps. If the amount of benzene in the condensate were added to the amount in the sorbent traps, the recovery would increase from 108 percent to approximately 150 percent of the expected value, which is in line with the other results for benzene at the 0.5-ppb test concentration.

TABLE D-7. SUMMARY OF WATER SAMPLE ANALYSES

Sample type	Run No.	Sample aliquot volume, ml	Total water sample volume, ml	Amount of target species in water sample,[a] nanograms		Normalized RIC area[b]
				Chloroform	Benzene	
Water from moisture generation apparatus	W3	15	48	c	0.3	46
	W4	6.0	50	c	c	81
	W7	7.5	49	c	c	34
	W8	5.0	44	c	c	83
	RR4	15.0	55	5.1	66.7	7122
	R7	9.5	70	0.7	2.9	86
	R8	15.0	31	0.8	1.2	47
Condensate and rinse of primary coil and flask	W6-ST444	9.0	20	c	c	172
	W7-ST333	9.5	20	c	14.1	194
	R7-NDY111	9.0	20	c	0.2	73
	R8-STZ444	15.0	30	1.4	4.8	1570

[a] No vinyl chloride, trichlorofluoromethane, carbon tetrachloride, or tetrachloroethylene was detected in any of the designated samples, except for Run RR4 sample, which contained an interferent to TCFM equivalent to approximately 2000 ng.

[b] Total RIC area divided by thousand-area units of internal standard. This value gives an overall indication of relative sample purity.

[c] None detected in sample aliquot.

Sample No. STZ444, the condensate sample for Run R8, contained approximately 1.4 ng of chloroform and 4.8 ng of benzene. These amounts compared with 41 ng of chloroform and 47 ng of benzene detected in the corresponding sorbent trap. If the amounts detected in the condensate were added to the amounts in the sorbent traps, the recoveries would increase from 88 percent to 91 percent of the expected value for chloroform and from 139 to 153 percent of the expected value for benzene. Neither of these changes is considered significant to the overall results. The normalized RIC area (1570) was also higher than for the other condensate samples (73 to 194), which indicates that the sample may have been contaminated to some degree. The results for the target compounds were probably not affected (except as just noted for chloroform and benzene).

The results of the water analyses indicate that some benzene and chloroform can be retained in the sample train condensate, but the amounts probably are not significant if the total amount of target in the sorbent traps is greater than approximately 50 ng.

Table D-8 presents the results of sample train blank checks that were conducted at the end of the laboratory validation. The test gas generation system was set up with zero air flowing through the dilution system and manifold. The quad sampling train was assembled in the same manner as for the tests conducted on the dry gas streams. Twenty liters of zero air was sampled by each train. These are designated in the table by the "BLK" prefix.

A separate sampling train was set up in the fourth position of the quad sample box and subjected to repeated leak-checks to assess the potential effect of contamination from ambient air when a leak exists in the train or

TABLE D-8. RESULTS OF SAMPLE TRAIN BLANKS COLLECTED AT THE END OF THE LABORATORY VALIDATION

Quad train position	Sample No.	Trap Nos.	Total amount of species in sample,[a] nanograms					
			Vinyl chloride	Trichloro-fluoro-methane	Chloroform	Carbon tetra-chloride	Benzene	Tetra-chloro-ethylene (perc)
1	BLK ST 111[b]	STT 126 STTC 35	ND	13.5	9.6	0.5	13.3	9.8
2	BLK ST 222[b]	STT 149 STTC 120	3.1	44.8	11.2	ND	543.8	30.2
3	BLK ND 333[b]	NDT 158 NDTC 197	0.1	13.0	3.0	1.1	77.8	5.8
4	BLK ND 444[a]	NDT 174 NDTC 92	1.4	7.2	3.7	ND	369.6	4.0
4	RLC Q4[c]	NDT 187 NDTC 158	1.1	15.7	4.6	0.4	66.8	5.2

[a] The presence of TCFM, benzene, and perc were generally confirmed by the mass spectra; however, the amounts of the other targets were mostly due to the presence of interferences.

[b] Each train sampled 20 liters of gas from the manifold that was being purged with zero air.

[c] This sample was subjected to repeated leak checks then removed from the train. No volume of sample gas was collected.

from residual matter in the train. It is recommended that the current protocol be revised to define a field blank as a set of traps taken to the field, assembled in the train, leak checked, and recovered as a typical sample.

The results shown in Table D-8 for vinyl chloride, chloroform, and carbon tetrachloride were quantitated by using their primary characteristic ions, even though positive identifications could not be made for the small amounts detected. The presence of perc was verified by the mass spectra of the samples. The presence of these four compounds in the sampling train blanks is probably due to bleeding of residual matter from the Teflon components or desorption from active sites on other components used in the test system. The amounts of VC, chloroform, carbon tetrachloride, and perc detected do not seem unreasonable. Values for TCFM also were probably related to residual matter in the test system components, but they were somewhat higher than what might be considered reasonable.

Results for benzene were extremely variable and could not be explained. The two very high values (540 and 370 ng) correspond to almost 10 times the expected value for a sample at the 0.5-ppb test condition, and are obviously outliers. These results are further evidence of the types of problems encountered when Tenax is used to measure benzene. Occasionally, a spurious analytical result for benzene is obtained that simply cannot be explained. Several times during the course of the laboratory validation, we encountered a calibration check point for benzene that was far higher than the expected response. Repeats of the calibration point generally resulted in acceptable results. A calibration point can be repeated if a spurious result is obtained, but a sample analysis cannot because the entire sample is consumed during the analysis. The presence of benzene as an inherent contaminant in Tenax probably is the principal reason for the variation observed in results for pretest sorbent trap blanks, GC/MS system blanks (due to Tenax in the analytical trap), calibrations made with sorbent traps, and analysis of sample sorbent traps. We have not been able to explain or resolve this problem completely. More consistent conditioning procedures have been developed for the ND traps, as presented in Section 3, which have helped to reduce the variation in pretest blank levels of benzene. Part of the problem with benzene results may be related to interference from the deuterated benzene internal standard used to quantify benzene. Another possibility is related to the GC/MS analytical equipment and procedures, which cause the analytical Tenax trap and the sample sorbent trap to be exposed to heat in the absence of purge flow. Thus, benzene inherently present in the Tenax may be released from internal sites, but would not be purged off the trap. Subsequent analysis would show benzene. We have not been able to verify this phenomenon, but higher benzene has been found in repeat analyses of the same sample trap, which tends to support this possibility. Recently we have had success (in limited instances) with the use of an extended total desorption and analysis cycle time that permits the sample sorbent traps to be purged until cooled after the sample is desorbed. In summary, benzene has yielded erratic results that have not been fully resolved.

The protocol includes a requirement to demonstrate recovery of target compounds by analyzing a pair of sorbent traps (a Tenax trap connected in series with a Tenax/charcoal trap) that have been spiked with a known amount of the target compounds. No specific procedures are given for spiking the traps. The spiked traps are purged with 20 liters of nitrogen (at 1 liter/min) to distribute the compounds onto the sorbents prior to analysis. The protocol does not specify if the internal standards are to be loaded onto the traps before or after the 20-liter purge. We performed a limited recovery study (as just described) by spiking the sorbent traps in the same manner as loading a standard. The internal standards were loaded after the 20-liter purge to simulate the way an actual sample would be treated. The ND traps in each sample were analyzed simultaneously. The ST traps were analyzed separately.

Results of the 20-liter recovery tests are presented in Table D-9.

TABLE D-9. RECOVERY OF TARGET COMPOUNDS FROM SPIKED SORBENT TRAPS AFTER PURGING WITH 20 LITERS OF NITROGEN
(percentage)

Nominal amount of each target loaded	Trap type	VC	TCFM	CF	CT	Benzene	Perc
100 ng	ND	103	51	68	64	115	98
250 ng	ND	102	39	90	52	108	92
250 ng	ST	90	17	30	32	75	85

The recoveries are biased by the loading techniques because target compounds in real samples are evenly distributed in the 20 liters of sample gas passing through the sorbent traps; whereas in the recovery tests, all of the target compounds were loaded in an initial spike. Loading the compounds as a spike of standard solution and then passing 20 liters of gas through the traps would tend to move some of the compounds well into the charcoal section of the second cartridge, from which they may not be recovered well by thermal desorption. A backup third Tenax trap was connected behind the Tenax/charcoal trap for each of the ND recovery tests. Analyses of these backup traps indicated that none of the target compounds broke through the Tenax and Tenax/charcoal traps. Surprisingly, it appears that all of the vinyl chloride was recovered, even though it almost certainly was all in the charcoal portion of the sorbent traps. These results suggest that VC can be thermally desorbed efficiently from charcoal, at least at the levels tested. This is inconsistent with overall results of the laboratory validation, which indicate that VC is not effectively measured with the VOST protocol. This discrepancy is currently not resolved.

The low recoveries for TCFM were not surprising because most of the amount loaded was expected to be in the charcoal portion of the sample, and the efficiency of thermally desorbing TCFM from charcoal was not expected to be high.

The low recoveries for chloroform and carbon tetrachloride were not expected; they may be a result of the compounds being pushed through the Tenax portion of the sample onto the charcoal. This would explain the erratic recoveries shown for chloroform when the ND traps were used because the calibration curves reflect desorption efficiency only for the Tenax, not the charcoal. The separate analyses of the ST traps indicated that over 90 percent of the chloroform detected and approximately half of the carbon tetrachloride were in the Tenax/charcoal trap.

Results for benzene and perc were as expected, indicating good recoveries.

The results of the 20-liter recovery tests point out the inadequacy of the specified recovery procedures. Alternative methods are available for loading the traps that would more closely simulate the way in which real samples are loaded. One way would be to make repeated injections of fractional amounts of the target compound solutions into the flash-evaporation device at equally spaced intervals while passing 20 liters of nitrogen through the traps. However, the errors associated with multiple injections are likely to be significant; therefore, this approach would have to be validated. Another way would be to use permeation tubes to generate an appropriate gas concentration in which 20 liters would contain the desired amount of target compound. The use of a permeation device would require additional equipment that may not be readily available to all users. Also, permeation devices might not be available for all compounds of interest. Audit gas cylinders could be used but are limited in availability. Either approach would more closely simulate a real sampling situation, but none would simulate the actual matrix effects.

The recovery test results also support the idea of keeping the Tenax and charcoal in separate traps. The same amount of total Tenax currently specified for both the front and backup traps could be combined into the front trap. One calibration curve would then be run for Tenax, and a separate curve would be run for charcoal traps. This would preclude simultaneous analyses of traps in pairs, but the separate calibration responses obtained would more accurately reflect the thermal desorption characteristics of Tenax and charcoal. Also, different analytical procedures could be used for the charcoal trap if warranted. The separate use of sorbents would be most beneficial for the more volatile compounds that are driven to the charcoal portion of the Tenax/charcoal traps currently used.

The quality assurance measures taken during this project were instrumental in obtaining the experience and data needed to evaluate the VOST protocol and recommend appropriate changes.

APPENDIX E

RUGGEDNESS TESTS

RUGGEDNESS TESTS

A series of tests (Runs R1 through R8) was conducted to determine if changes in any of several selected variables had a significant impact on results obtained by the VOST method, and if so, which should be selected for further evaluation. The procedures outlined in Youden's Ruggedness Tests* were used as guidelines. In accordance with Youden's approach, seven variables were tested at two levels in eight different combinations, which yielded a 1/16 replicate factorial experiment. Whether a change in a variable has a significant effect on results should have been determined for each compound; however, a limitation of Youden's test is that interactions among variables cannot be discerned. Duplicate trains were used to conduct each of the eight runs in an attempt to enhance the interpretive power of Youden's tests. Also, the expected response from each run was known.

Table E-1 presents seven variables and levels of each that were selected for the VOST ruggedness test.

TABLE E-1. VARIABLES AND LEVELS FOR VOST RUGGEDNESS TEST

Variables	Letter designation	Levels	
		Level 0	Level 1
POHC concentration	A	0.5 ppb	15 ppb
Moisture	B	~25%	Dry
Sampling rate	C	0.5 liter/min	1.0 liter/min
Gas temperature at inlet to first trap	D	≅30°C	≤20°C
Sorbent condition	E	Reused[a]	New
Sample volume	F	5 liters	20 liters
Trap configuration	G	ST	ND

[a] Tenax only; new charcoal was used in all cases.

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[*] Statistical Manual of the Association of Official Analytical Chemists, Youden and Steiner, 1975.

Moisture was included because many hazardous waste incineration facilities at which the VOST protocol has been and will be used have exhaust gas streams saturated with moisture. Sampling rate, sample volume, reagent condition, and trap configuration values were included because the protocol permitted these variations. The inlet gas temperature was selected to determine if the protocol limit of 20°C was critical for low boiling-point compounds.

The ruggedness tests incorporated several procedural changes to the nominal VOST conditions, as designated in the previous description of selected variables. For some of the runs room-temperature water instead of ice water was circulated through the condenser coils so that the temperature of the sample gas exiting the first condenser was approximately 27°C instead of less than 20°C. Also, sampling rates of 0.5 liter/min and sample volumes of 5 liters were designated instead of the nominal conditions of 1 liter/min and 20 liters. The various combinations of these parameters required by the ruggedness test plan were achieved by varying the sampling times between 5, 10, 20, or 40 minutes instead of the nominal 20 minutes.

One other change for the ruggedness tests involved the use of "new" and "used" Tenax. The "new" Tenax was defined as having been prepared by normal procedures (see Appendix B) and having not been used before to collect any type of sample. "Used" Tenax was defined as having been prepared initially by normal procedures and having been used to collect one of the test samples (not a blank sample). After GC/MS analysis, the "used" Tenax was reprepared by normal procedures and made ready for the designated ruggedness tests. These procedures applied only to the Tenax, as the protocol required new charcoal to be used in all cases. Thus, in the Tenax/charcoal traps designated as "used", the charcoal portion was replaced with new charcoal prior to repreparation.

In addition to the procedural changes just described, other changes to the sampling equipment and procedures were made for the wet runs, as described in Section 3. As indicated, several different variations of the wet test gas system were used until the final system previously shown in Figure 3-8 was developed. For Runs R7 and R8, the flow of sample gas through the water flask was reversed; that is, the gas from the manifold entered through the side tube and left through the impinger stem. Also, the line from the manifold to the flask was not heated. For Runs RR4 (a repeat of R4) and R3, a Teflon impinger was used instead of a glass flask; therefore, a hot plate was not used. Also, the sample flow entered through the side tube and exited through the impinger stem. For Run RR4, the sample line from the manifold was heated, but for Run R3 it was not. A Teflon impinger was also used for R4, but it was heated only around the water level, not the entire container. Gas flow entered through the side tube, but the inlet gas line was not heated.

Test Design

The letter and number designations for the variables (see Table E-1) are used to simplify the design of the ruggedness test as presented in Table E-2.

TABLE E-2. DESIGN OF YOUDEN'S RUGGEDNESS TEST

	Run No. and combination of variable levels							
Variable	1	2	3	4	5	6	7	8
A	1	1	1	1	0	0	0	0
B	1	1	0	0	1	1	0	0
C	1	0	1	0	1	0	1	0
D	1	1	0	0	0	0	1	1
E	1	0	1	0	0	1	0	1
F	1	0	0	1	1	0	0	1
G	1	0	0	1	0	1	1	0
Observed result	s	t	u	v	w	x	y	z

The combination of variable levels is shown for each of the eight test runs. For example, the value of Variable C (sampling rate) in Run 1 is "1" (for the Level 1 value of 1 liter/min) and in Run 2 "0" (for the Level 0 value of 0.5 liter/min). The observed result for each run is also labeled with a letter designation to simplify data reduction. Because duplicate sampling trains were used, there were two observed results for each run, e.g., s_1 for Train 1 and s_2 for Train 2.

The full potential of the ruggedness tests was not realized for all of the target compounds because there is a strong interdependence between runs in Youden's analysis and several of the runs were void. Project constraints did not permit most of the voided runs to be repeated. For the reader's information, a brief outline of Youden's data reduction procedure is given even though it was not actually used for all compounds. Because concentration of the target compounds was one of the variables, the observed results were normalized by dividing them by the expected concentrations to avoid the interpretation being biased by the high concentrations. Basically, the response due to a given level of a given variable is determined by combining the observed results of selected runs so that the effects of the other variables are cancelled. Table E-3 presents the formulas for calculating the response of each variable level.

TABLE E-3. FORMULAE FOR CALCULATING RUGGEDNESS TEST VARIABLE RESPONSES

Variable	Level 0 response	Level 1 response
A	$(w + x + y + z)/4 = A_0$	$(s + t + u + v)/4 = A_1$
B	$(u + v + y + z)/4 = B_0$	$(s + t + u + x)/4 = B_1$
C	$(t + v + x + z)/4 = C_0$	$(s + u + w + y)/4 = C_1$
D	$(u + v + w + x)/4 = D_0$	$(s + t + y + z)/4 = D_1$
E	$(t + v + w + y)/4 = E_0$	$(s + u + x + z)/4 = E_1$
F	$(t + u + x + y)/4 = F_0$	$(s + v + w + z)/4 = F_1$
G	$(t + u + w + z)/4 = G_0$	$(s + v + x + y)/4 = G_1$

For ease of distinction the responses are labeled in terms of the variable and its level using the designations shown in Table E-1. Thus, "C_0" is the average response of Variable C at Level 0 (sampling rate of 0.5 liter/min). Because duplicate trains were used, two responses can be calculated for each case. By comparing the responses at each level of a variable (e.g., calculating the difference between response A_0 and A_1), the effect of changing the variable is determined. The magnitude of the differences between levels for all of the variables is compared to determine if the effect of any of the variables is more significant than any of the others.

The following subsections summarize the sampling data, analytical data, concentration results, and interpretation of the results. For the compounds where Youden's data reduction procedure could not be applied, some useful information was obtained by comparing the results of Runs R1 through R8 with the results from the precision and accuracy runs (Q and W series).

Sampling Data Summary

Eight paired runs, Runs R1 through R8, were conducted using the various combinations of parameters as outlined in Tables E-1 and E-2. A repeat of Run R4, Run RR4, was conducted because the actual parameter conditions for Run R4 were not close enough to desired conditions. This was the only case in which a voided run was able to be repeated. The results of RR4 were used in all subsequent data reduction. All samples were analyzed within one week of collection. Results of blank samples were shown previously in Section 4.

Table E-4 presents the data for the generation of dry test gases. As previously described in Section 3, the addition of moisture for Runs R3, R4, RR4, R7, and R8 did not affect operation of the dry test gas generation system.

TABLE E-4. SUMMARY OF DILUTION SYSTEM DATA AND EXPECTED SPECIES CONCENTRATION FOR RUGGEDNESS TESTS

Date (1984)	Run No.	Average dilution system flow rates, liter/min			Expected species concentrations at manifold											
					Vinyl chloride		Trichloro-fluoromethane		Chloroform		Carbon tetrachloride		Benzene		Tetra-chloroethylene	
		Group 1 cylinder[a]	TCFM cylinder[b]	Total to manifold[c]	ppb	ng/liter	ppb	ng/liter	ppb	ng/liter	ppb	ng/liter	ppb	ng/liter	ppb	ng/liter
5/22	R1	1.339	0.990	5.937	16.12	41.92	14.97	85.65	13.67	67.88	14.84	94.94	14.98	48.65	15.43	106.4
5/22	R2	1.333	0.987	5.891	16.18	42.06	15.04	86.05	13.71	68.10	14.89	95.26	15.02	48.81	15.48	106.8
5/23	R3	1.344	0.998	5.921	16.23	42.19	15.14	86.57	13.76	68.32	14.94	95.55	15.07	48.96	15.53	107.1
5/24	R4	1.342	0.998	5.944	16.14	41.97	15.08	86.24	13.68	67.95	14.86	95.04	14.99	48.70	15.44	106.6
5/25	RR4	1.358	0.999	5.994	16.20	42.11	14.97	85.60	13.73	68.19	14.91	95.37	15.04	48.87	15.50	106.9
Combined statistics		$\bar{x}$, ng/liter σ, ng/liter % RSD				42.07 0.113 0.27		85.97 0.449 0.52		68.12 0.185 0.27		95.28 0.256 0.27		48.82 0.130 0.27		106.8 0.294 0.28
5/30	R5	0.046	0.034	5.934	0.55	1.44	0.51	2.94	0.47	2.33	0.51	3.26	0.51	1.67	0.53	3.66
5/30	R6	0.046	0.034	6.021	0.55	1.42	0.51	2.90	0.46	2.30	0.50	3.22	0.51	1.65	0.52	3.61
5/31	R7	0.047	0.033	5.970	0.56	1.46	0.50	2.84	0.48	2.37	0.52	3.31	0.52	1.70	0.54	3.72
5/30	R8	0.047	0.034	5.961	0.56	1.46	0.51	2.93	0.48	2.37	0.52	3.32	0.52	1.70	0.54	3.72
Combined statistics		$\bar{x}$, ng/liter σ, ng/liter % RSD				1.44 0.019 1.3		2.90 0.045 1.6		2.34 0.034 1.4		3.28 0.046 1.4		1.68 0.024 1.4		3.68 0.053 1.4

[a] Undiluted cylinder concentrations used to calculate expected values are 71.5 ppb vinyl chloride; 60.6 ppb chloroform; 65.8 ppb carbon tetrachloride; 66.4 ppb benzene; and 68.4 ppb tetrachloroethylene in nitrogen.

[b] Undiluted cylinder concentrations used to calculate expected values is 89.8 ppb trichlorofluoromethane in nitrogen.

[c] Includes dilution air cylinder gas flow which is not shown and both cylinders of known gases.

The gas flow rates shown for each run are based on the average of pre- and post-run bubble meter measurements. Flows were very stable, and the difference in flow measurements over a given run was no greater than the differences between runs. Expected concentrations of the target compounds are shown in parts per billion and nanograms per liter for each run. The mean concentration, standard deviation, and relative standard deviation (percentage) are shown to demonstrate the comparability of expected concentrations for each group of similar runs. Runs R1 through RR4 were conducted at a nominal test gas concentration of 15 ppb. As indicated, the relative standard deviation was less than 1 percent for any one compound over these five runs. Runs R5 through R8 were conducted at a nominal concentration of 0.5 ppb. The relative standard deviation for any one compound over these four runs was no more than 1.6 percent. These results demonstrate the reproducibility of the expected concentrations in the dry gas streams during the ruggedness test. The concentrations also compared well with the other similar tests (Runs Q1 through Q8 and W1 through W8).

Table E-5 summarizes the sample collection data for these runs. Each sampling train was assigned a sample number as indicated in the table. Individual sample fractions (the Tenax trap, backup Tenax/charcoal trap, and any condensate) were identified by adding a suffix or trap number to the sample number. The sample number consisted of two letters designating the trap configuration, a one-letter designation equivalent to the observed result (see Table E-2), and three numbers identifying the probe liner, sampling train position within the quad sample box, and the meter control unit used to collect the sample. When preceded by the run number, each sample number represented a unique sample. The particular combination of trap type and train components were rotated to avoid any inherent biases.

TABLE E-5. SUMMARY OF SAMPLE TRAIN CONDITIONS FOR RUGGEDNESS TESTS

Date (1984) and time (24-h)	Run No.	Sample No.	Data designation (D or M)[a]	Variable conditions								Related sampling conditions			
				Nominal concentration, ppb	Moisture, %	Average sampling rate, liter/min	Gas temperature at inlet to first trap, °C		Sorbent condition	Metered sample volume, liters	Trap configuration	Net sample time, min	Average probe temperature, °C	Maximum vacuum, in.Hg	Post-test leak rate, in.Hg/min
							Avg.	Max.							
5/22 1503	R1		D	15	Dry	1.00	≤20		New	20.00	ND	20.0			
		MDS111	M	13-16[b]	Dry	1.05	12.2	13.9	New	20.03	ND	19.0	119	<1.0	<0.1
		MDS333	M			1.02	11.1	13.3	New	20.02	ND	19.6	116	3.2	<0.1
5/22 1504	R2		D	15	Dry	0.50	≤20		Reused	5.00	ST	10.0			
		STT222	M	13-16[b]	Dry	0.52	10.9	11.1	Reused	5.01	ST	9.6	115	<1.0	0.1
		STT444	M			0.49	9.4	9.4	Reused	5.03	ST	10.2	118	3.0	<0.1
5/23 1509	R3		D	15	25	1.00	~30		New	5.00	ST	5.0			
		STU334	M	13-16[b]	18	0.91	27.0	27.2	New	4.96	ST	5.4	104	2.5	<0.1
		STU112	M			0.98	27.0	27.2	New	5.00	ST	5.1	104	<2.0	<0.1
5/24 1050	R4		D	15	25	0.50	~30		Reused	20.00	ND	40.0			
		MDV221	M	13-16[b]	9	0.44	24.9	25.6	Reused	20.02	ND	45.1	120	5.5	<0.1
		MDV443	M			0.52	25.1	25.6	Reused	20.01	ND	38.1	120	2.0	<0.1
5/25 1540	RR4[d]		D	15	25	0.50	~30		Reused	20.00	ND	40.0			
		MDV221	M	13-16[b]	17	0.49	29.1	29.4	Reused	19.99	ND	40.5	120	2.2	<0.1
		MDV443	M			0.51	29.2	30.0	Reused	20.02	ND	39.4	120	2.2	<0.1
5/30 1330	R5		D	0.5	Dry	1.00	~30		Reused	20.00	ST	20.0			
		STW112	M	0.46-0.56[c]	Dry	1.00	25.8	26.1	Reused	20.00	ST	20.0	124	<2.0	<0.1
		STW221	M			1.05	25.9	26.1	Reused	20.00	ST	19.0	124	<2.0	<0.1
5/30 1331	R6		D	0.5	Dry	0.50	~30		New	5.00	ND	10.0			
		MDX334	M	0.46-0.56[c]	Dry	0.49	25.6	25.6	New	5.00	ND	10.2	124	2.0	<0.1
		MDX443	M			0.48	25.4	25.6	New	5.03	ND	10.4	124	2.0	<0.1
5/31 1318	R7		D	0.5	25	1.00	≤20		Reused	5.00	ND	5.0			
		MDY111	M	e	e	1.02	11.1	11.7	One new, one re-used[f]	5.09	ND	5.0	131	2.0	>0.1[e]
		MDY222	M	0.46-0.56[c]	24	0.86	11.7	12.2	Reused	4.97	ND	5.8	131	2.0	<0.1
5/30 1714	R8		D	0.5	25	0.50	≤20		New	20.00	ST	40.0			
		STZ333	M	0.46-0.56[c]	52	0.50	19.0	20.6	New	20.00	ST	40.0	117	<2.0	<0.1
		STZ444	M			0.48	19.6	21.7	New	20.00	ST	42.0	117	2.0	<0.1

[a] D = Desired; M = Measured.

[b] The expected concentration of each compound in the dry test gas was between 13 and 16 depending on the cylinder concentration.

[c] The expected concentration of each compound in the dry test gas was between 0.46 and 0.56 depending on the cylinder concentration.

[d] Run RR4 is a repeat of Run R4.

[e] Run was void because the Teflon connector between the 4-way valve and condenser inlet melted sometime during the run.

[f] New Tenax trap; reused Tenax/charcoal trap.

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For each of the seven variables in the ruggedness test a distinction is made in Table E-5 between the desired condition (D) and the actual, measured condition (M) during the run. Values for related sampling conditions are also shown. Because of the interdependence of results on Youden's data analysis procedure, it was further desired that the level of a given variable be as consistent as practically possible for all of the runs in which that level was used. As shown in the table, relative consistency was achieved for all of the variables except moisture content and sampling rate. Also, in the case of Run R7, Sample No. NDY111, a reused Tenax trap was not available. This is insignificant because this sample was void. The differences in moisture content were related to changes that were made to the apparatus for adding moisture to the sample stream. Changes were made as described previously in Subsection 3.2.3 until reproducible moisture contents were obtained.

The moisture content for Run R4 was checked immediately upon completion of the run. Because the moisture content was low (~9 percent compared with ~18 percent for Run R3) and the schedule permitted, a repeat of the run was made (Run RR4) incorporating changes to the moisture apparatus. As indicated, comparable moisture values were obtained.

It would have been desirable to repeat Run R7 (because of the relatively high moisture and failure of one of the paired trains to pass the post-test leak check) and Run R8 (high moisture), but the schedule and budget constraint did not permit it. Extra sorbent traps were not available for repeating these tests, as they had been available for Run RR4; therefore, additional sorbent traps would have had to be conditioned and blank-checked prior to repeating the tests. It should be noted that neither of the samples in Run R7 contained any noticeable condensation in the primary coil or sorbent trap at the end of the run, despite the apparent calculated moisture content of 24 percent.

The average sampling rates for two of the samples, Run R4, Sample No. NDV221, and Run R7, Sample No. NDY222, were more than 10 percent different from desired values because of problems encountered in adjusting the sampling rates. For these samples the sampling time was extended so that the desired volume was obtained.

The average probe temperatures were all above the moisture dewpoint. All post-test leak rates were within acceptable limits except for Run R7, Sample No. NDY111, in which a segment of heated Teflon line melted at some point during the run.

Laboratory Data Summary

Table E-6 presents the GC/MS analysis results for each sample sorbent trap. The unique trap identification numbers shown include the ND or ST designation, a "T" for the Tenax traps or a "TC" for the Tenax/charcoal backup traps, and the individual serial numbers etched on the traps. An "R" in the serial number means the Tenax portion of the trap was reused; however, the "R" was not etched in the glass. The amounts of target compounds shown for each trap were taken directly from the GC/MS quantitation lists for each analysis and summed to determine the total for a given sample. The percent of each target compound collected on the Tenax trap was calculated to evaluate the effectiveness of the Tenax trap in collecting the sample, or the potential for breakthrough.

Most of the analyses were performed in accordance with planned procedures; however, a few analyses incorporated slight modifications. Analyses of Traps No. ST-TC-161 and ST-T-164 (from the first and second trains in Run R3) were made with the wrong amount of internal standards loaded onto the traps.

TABLE E-6. ANALYTICAL RESULTS FOR RUGGEDNESS TESTS

Date (1984)	Run No.	Sample No.	Trap No.	Amount of species in sample																	
				Vinyl chloride			Trichloro-fluoromethane			Chloroform			Carbon tetrachloride			Benzene			Tetrachloro-ethylene (perc)		
				ng per trap	total ng	% on Tenax	ng per trap	total ng	% on Tenax	ng per trap	total ng	% on Tenax	ng per trap	total ng	% on Tenax	ng per trap	total ng	% on Tenax	ng per trap	total ng	% on Tenax
5/22	R1	HDS111	HD-T-95 HD-TC-111	2.3 337.2	339.5	0.7	411.7 726.5	1,138	36.2	1446 9.2	1455	99.4	1200 464.4	1664	75.0	1080 4.7	1085	99.6	2209 11.2	2220	99.5
5/22	R1	HDS333	HD-T-57 HD-TC-129	5.1 600.5	605.6	1.0	427.7 788.0	1,216	35.2	1358 5.1	1363	99.6	1213 550.2	1763	68.8	966.2 6.4	972.6	99.3	2740 9.6	2750	99.6
5/22	R2	STT222	ST-T-R111 ST-TC-R40	12.0 3.9	15.9	75.5	203.2 a	203.2	100	361.0 a	361.0	100	330.0 a	330.0	100	244.2 1.0	245.2	99.6	461.6 16.7	478.3	96.5
5/22	R2	STT000	ST-T-R61 ST-TC-R142	6.3 26.4	32.7	19.3	232.3 34.1	266.4	87.2	302.2 5.5	307.7	98.2	335.2 17.4	352.6	95.1	247.4 3.7	251.1	98.5	462.3 17.7	480.0	96.3
5/23	R3	STU330	ST-T-159 ST-TC-161^b	1.6 13.7	15.3	10.4	286.0^c 142.0^c	428.0	66.7	400.7 a	400.7	100	332.3 28.6	360.9	92.1	521.7 10.8	532.5	98.0	731.4 2.2	733.6	99.7
5/23	R3	STU112	ST-T-104^b ST-TC-176	0.7 7.5	8.2	8.5	242.7^c 104.8	347.5	69.8	287.4 21.5	308.9	93.0	245.0 48.9	293.9	83.4	406.6^c 33.4	440.0	92.4	517.0 23.9	540.9	95.6
5/23	R4	HDV221	HD-T-R07 HD-TC-R120	0.7 294.8	295.5	0.2	604.7^c 1102	1,707	35.4	1144 131.7	1276	89.6	1198 295.4	1493	80.2	1146 25.9	1172	97.8	2747.4 10.3	2758	99.6
5/23	R4	HDV003	HD-T-R126 HD-TC-R110	1.3 211.3	212.6	0.6	555.9^c 1159	1,715	32.4	1211 140.0	1351	89.6	1228 472.4	1700	72.2	1216 25.0	1241	98.0	2782.4 11.3	2794	99.6
5/25	R4R	HDV221	HD-T-R33 HD-TC-R85	N/A^d	335.6^c	N/A	N/A	15,000^e	N/A	N/A	1111	N/A	N/A	1366	N/A	N/A	877.4	N/A	N/A	2471	N/A
5/25	R4R	HDV003	HD-T-R37 HD-TC-R50	a 342.4	342.4^c	0	1106 3114	4,220^e	26.2	1061 261.9	1323	80.2	1225 493.0	1718	71.3	1088 216.4	1304	83.4	2701 173.0	2906	95.0
5/31	R5	STW112	ST-T-4 ST-TC-142	0.2 9.5	9.7	2.1	18.2 10.0	28.2	64.5	39.3 5.1	44.4	88.5	39.8 9.9	49.7	80.1	30.2 3.7	33.9	89.1	68.6 8.8	77.4	88.6
5/31	R5	STW221	ST-T-111 ST-TC-21	0.9 8.3	9.2	9.8	20.2 13.7	33.9	59.6	36.3 7.8	44.1	82.3	42.4 11.0	53.4	79.4	28.3 4.3	32.6	86.8	72.3 10.1	82.4	87.7
5/31	R6	HDR443	HD-T-31 HD-TC-19	1.5 2.6	4.1	36.6	11.2 7.8	19.0	58.9	11.3 4.8	16.1	70.2	15.8 0.2	16.0	98.8	8.6 10.9	19.5	44.1	18.7 5.1	23.8	78.6
5/31	R6	HDR330	HD-T-30 HD-TC-9	1.0 2.7	3.7	27.0	11.8 8.4	20.2	58.4	12.0 3.8	15.8	75.9	10.3 a	10.3	100	25.1 4.3	29.4	85.4	20.2 4.5	24.7	81.8

(continued)

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TABLE E-6 (continued)

				Amount of species in sample																	
				Vinyl chloride			Trichloro-fluoromethane			Chloroform			Carbon tetrachloride			Benzene			Tetrachloro-ethylene (perc)		
Date (1984)	Run No.	Sample No.	Trap No.	mg per trap	total mg	% on Tenax	mg per trap	total mg	% on Tenax	mg per trap	total mg	% on Tenax	mg per trap	total mg	% on Tenax	mg per trap	total mg	% on Tenax	mg per trap	total mg	% on Tenax
6/1	87	MDV111[f]	MD-T-22 MD-TC-876	0.3 10.0	10.3[f]	2.9	512.9 332.1	845.0[f]	60.7	18.3 3.6	21.9[f]	83.6	11.1 2.2	13.3[f]	83.5	320.8 11.5	332.3[d]	96.5	31.0 4.3	35.3[f]	87.8
6/1	87	MDV222	MD-T-82 MD-TC-887	0.2[c] [a]	0.2	100	10.7 15.8[c]	26.5	40.4	32.6 7.2	39.8	81.9	13.7 4.8	18.5	74.1	8.1 4.2[c]	12.3	65.9	19.2 2.9	22.1	86.9
6/11	88	ST2333	ST-T-165 ST-TC-64	1.8 13.2	15.0	12.0	18.4 12.5	30.9	59.5	40.5 5.6	46.1	87.9	49.4 9.9	59.3	83.3	38.4 7.1	45.5	84.4	80.6 7.9	88.5	91.1
6/1	88	ST2444	ST-T-125 ST-TC-173	1.6 8.8	10.4	15.4	17.0 12.6	29.6	57.4	32.9 8.0	40.9	80.4	39.6 10.5	50.1	79.0	39.3 7.3	46.6	84.3	84.7 6.7	91.4	92.7

[a] None detected.

[b] Improper amount of internal standard was added to sample; therefore, representative internal standard values were used to calculate species amounts.

[c] Quantitation of species amount may be biased high by the presence of interferences.

[d] Not applicable, the sample was analyzed as a pair.

[e] Quantitation of TCFM was biased high by chlorofluorocarbon contamination from the Teflon impinger used in the moisture generation system.

[f] Results void because a segment of heated Teflon lined in the sample train melted at some point during the run.

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Tabulated amounts were recalculated using average internal standard response data for other analyses that particular day and the current average calibration response factors. The first train in Run R3 has questionable values for the very volatile compound which are collected to a greater extent on the backup Tenax/charcoal trap. The second train from Run R3 has questionable values for the less volatile compounds, which are collected on the front Tenax trap. Sample traps from Run RR4, Sample No. NDV221, were analyzed as a pair instead of separately in order to save analysis time.

As indicated in Table E-6, the presence of interferences may have biased results of several samples from the wet runs for VC, TCFM, and benzene. The interferences may have resulted from contaminants arising from the Teflon impingers or connecting lines used in the moisture generation apparatus. The potential presence of interferents was determined by examining the mass spectral fragmentation patterns of the GC/MS scans of the target compounds in the samples. For the indicated samples the spectra included ions that were either foreign to the target compound, or the primary and secondary ions were present in abnormal relative abundances, or both. The potential effect of the interferences was to bias results high. For Run RR4 interferences to TCFM were definitely present, probably from contaminants diffused in the walls of the Teflon impingers used in the moisture generation apparatus. The impinger had been replaced between Run R4 and Run RR4 because of leak-check problems with the impinger used initially in Runs R3 and R4. The impinger in the moisture generation apparatus for Run RR4 was not new and had been used previously in a situation involving a variety of chlorofluorocarbons. Even though the impinger had been acid-washed and oven-dried prior to use in the moisture apparatus, it obviously still contained material diffused in the Teflon, as exhibited by the wide variety of chlorofluorocarbons identified in the Run RR4 sorbent samples. Subsequent to this run, glass flasks were used in the moisture apparatus instead of Teflon. This experience supports the need to exercise caution when using Teflon or other permeable materials.

As previously noted, Run R7, Sample No. NDY111, was void because the Teflon connector between the four-way valve in the sample train and the condenser coil melted at some point during the run. The results for this sample suggest that the primary interferences to the sample were TCFM and benzene contamination, and the Teflon piece probably melted near the end of the run.

A meaningful evaluation of the percentage of material collected on the Tenax traps was not possible for the ruggedness test samples because of the different combination of sampling parameters and the potential interferences to many of the VC and TCFM results. In general, the percentage of material on the front Tenax trap seemed to agree with results for the precision and accuracy samples, with a notable exception. All of the VC detected in Sample No. NDY222 (for Run R7) was on the Tenax trap. It should be pointed out that a possible interferent (and high bias) was present in this sample and the measured concentration (as shown in a later table) yielded a much higher percent of expected value than exhibited by other samples.

Concentration Data Summary

Table E-7 presents the total target compound concentrations in each sample. The metered dry gas sample volume for each run is given in liters corrected to 20°C and 760 mmHg. Sample concentrations were calculated by dividing the total amount of target detected on the Tenax and Tenax/charcoal traps by the standard sample volume. The indicated samples were biased as just described in the laboratory data summary.

TABLE E-7. SAMPLE CONCENTRATIONS FOR RUGGEDNESS TESTS
(ng/liter)

Date (1984)	Run No.	Sample No.	Sample volume, liters, at STP[a]	Vinyl chloride	Trichloro-fluoromethane	Chloroform	Carbon tetrachloride	Benzene	Tetrachloro-ethylene (perc)
5/22	R1	HDS111	19.41	17.49	58.63	74.96	84.70	51.93	114.4
		HDS333	19.29	25.17	63.04	70.66	91.39	50.42	117.0
5/22	R2	STT222	4.82	3.11	42.16	75.06	68.46	50.87	98.82
		STT444	4.90	6.67	54.37	79.12	71.96	51.24	97.96
5/23	R3	STU334	4.89	3.13	87.65[b]	81.94	73.80	108.9[b]	150.0
		STU112	4.87	1.68	71.36[b]	63.43	60.35	89.94[b]	111.1
5/24	R4	HDV221	19.96	14.80	89.53[b]	63.93	74.80	58.72	113.1
		HDV443	19.94	10.66	86.01[b]	67.76	82.26	62.24	115.0
5/25	RR4	HDV221	19.26	27.80[b]	781.3[c]	57.68	70.92	45.56	128.3
		HDV443	19.29	17.75[b]	218.8[c]	65.58	89.06	67.60	150.6
5/31	R5	STW112	19.60	0.49	1.44	2.26	2.54	1.73	3.95
		STW221	19.59	0.50	1.73	2.27	2.72	1.66	4.21
5/31	R6	HDX443	5.00	0.82	3.80	3.22	3.20	3.90	4.76
		HDX334	5.03	0.74	4.02	3.14	3.64	5.84	4.91
6/1	R7	HDY111[d]	4.98	2.07[d]	169.7[d]	4.40[d]	2.67[d]	66.73[d]	7.09[d]
		HDY222	4.92	1.67[b]	5.39[b]	8.09	3.76	2.50[b]	4.49
6/1	R8	STZ333	19.49	0.77	1.58	2.36	3.04	2.33	4.54
		STZ444	19.64	0.53	1.51	2.08	2.55	2.37	4.65

[a] Standard conditions of 20°C and 760 mmHg.

[b] Interferences in mass spectra.

[c] Quantitation biased by chlorofluorocarbon contamination in moisture apparatus.

[d] A segment of heated Teflon sample line melted at some point during the run, thus contaminating the sample and resulting in failure to pass the post-test leak check.

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The data are difficult to interpret because of the different combinations of sampling parameters in each run. To assist in the comparison of the ruggedness test data with the precision and accuracy run data, a summary of precision results for the ruggedness test paired samples is presented in Table E-8. The mean, standard deviation, and percentage RSD are shown for each paired run, excluding the results for the biased samples. In addition, Table E-9 presents the normalized sample concentrations, again excluding biased sample results. The normalized concentration is the measured concentration divided by the expected concentration of the target compound in the sampled dry gas stream (from Table E-4). Multiplying the normalized concentration by a factor of 100 would convert it to percent of expected value (EV), a measure of the recovery of the compound.

Interpretation of Results

At least one value is necessary for each run in order to use Youden's data reduction method. From the values listed in Table E-9, only CF, CT, and perc are capable of being analyzed in this manner. Some information can be obtained for the other compounds by comparison to Runs Q1 through Q8 and W1 through W8.

Chloroform--

The results of Youden's data reduction procedure for chloroform (and also carbon tetrachloride and tetrachloroethylene) are presented in Tables E-10 and E-11. The normalized responses for each level (0 and 1) on each variable are presented for each duplicate train in Table E-10. These responses were calculated using the normalized concentrations for each run from Table E-9 and the equations in the table of response formulas (Table E-3). The difference in

TABLE E-8. SUMMARY OF PRECISION DATA FOR RUGGEDNESS TEST PAIRED SAMPLES

		Vinyl chloride			Trichloro-fluoromethane			Chloroform			Carbon tetrachloride			Benzene			Tetrachloro-ethylene (perc)		
Date (1984)	Run No.	$\bar{x}$ (ng/liter)	σ (ng/liter)	% RSD	$\bar{x}$ (ng/liter)	σ (ng/liter)	% RSD	$\bar{x}$ (ng/liter)	σ (ng/liter)	% RSD	$\bar{x}$ (ng/liter)	σ (ng/liter)	% RSD	$\bar{x}$ (ng/liter)	σ (ng/liter)	% RSD	$\bar{x}$ (ng/liter)	σ (ng/liter)	% RSD
5/22	R1	21.33	5.43	25.4	60.84	3.12	5.1	72.81	3.04	4.2	88.04	4.73	5.4	51.18	1.08	2.1	115.7	1.84	1.6
5/22	R2	4.89	2.52	51.5	48.26	8.63	17.9	77.09	2.87	3.7	70.21	2.47	3.5	51.06	0.26	0.5	98.39	0.61	0.6
5/23	R3	2.40	1.02	42.5	a	a	a	72.68	13.09	18.0	67.08	9.51	14.2	108.9	b	b	130.6	27.51	21.1
5/24	R4	12.73	2.93	23.0	a	a	a	65.84	2.70	4.1	80.03	7.40	9.2	60.48	2.49	4.1	114.0	1.34	1.2
5/25	RR4	a	a	a	a	a	a	63.13	7.71	12.2	79.99	12.83	16.0	56.58	15.58	27.5	139.4	15.77	11.3
5/31	R5	0.50	0.01	20.0	1.58	0.20	12.6	2.26	0.01	0.4	2.63	0.13	4.9	1.70	0.05	2.9	4.08	0.18	4.4
5/31	R6	0.78	0.06	7.7	3.91	0.16	4.1	3.18	0.06	1.9	3.42	0.31	9.1	4.87	1.37	28.1	4.84	0.11	2.3
6/1	R7	a	a	a	a	a	a	8.09	b	b	3.76	b	b	a	a	a	4.49	b	b
6/1	R8	0.65	0.17	26.2	1.54	0.05	3.2	2.22	0.20	9.0	2.80	0.35	12.5	2.35	0.03	1.3	4.60	0.08	1.7

[a] Both samples considered invalid.

[b] One sample considered invalid.

TABLE E-9. NORMALIZED SAMPLE CONCENTRATIONS FOR RUGGEDNESS TESTS[a] (ng/liter)

Date (1984)	Run No.	Sample No.	Sample volume, liters at STP[a]	Vinyl chloride	Trichloro-fluoromethane	Chloroform	Carbon tetrachloride	Benzene	Tetrachloro-ethylene (perc)
5/22	R1	HDS111 HDS333	19.41 19.29	0.417 0.600	0.684 0.736	1.10 1.04	0.892 0.963	1.07 1.04	1.08 1.10
5/22	R2	STT222 STT444	4.82 4.90	0.074 0.158	0.490 0.632	1.10 1.16	0.719 0.755	1.04 1.05	0.925 0.917
5/23	R3	STU334 STU112	4.89 4.87	0.074 0.040	b b	1.20 0.928	0.772 0.632	2.22 b	1.40 1.04
5/24	R4	HDV221 HDV443	19.96 19.94	0.353 0.254	b b	0.941 0.997	0.787 0.897	1.20 1.28	1.06 1.08
5/25	RR4	HDV221 HDV443	19.26 19.29	b b	c c	0.846 1.01	0.744 0.934	0.932 1.38	1.20 1.41
5/31	R5	STW112 STW221	19.60 19.59	0.340 0.347	0.490 0.588	0.970 0.974	0.779 0.834	1.04 0.994	1.08 1.15
5/31	R6	HDX443 HDX334	5.00 5.03	0.577 0.521	1.31 1.39	1.40 1.36	0.994 1.13	2.36 3.54	1.32 1.36
6/1	R7	HDY111 HDY222	4.98 4.92	d b	d b	d 3.41	d 1.142	d b	d 1.21
6/1	R8	STZ333 STZ444	19.49 19.64	0.527 0.363	0.539 0.515	0.996 0.878	0.916 0.768	1.37 1.39	1.22 1.25

[a] Measured concentrations normalized by dividing them by expected concentrations.

[b] Interference in mass spectra.

[c] Quantitation biased by chlorofluorocarbon contamination in moisture apparatus.

[d] A segment of heated Teflon sample line melted at some point during the run, thus contaminating the sample and resulting in failure to pass the post-test leak check.

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TABLE E-10. SUMMARY OF NORMALIZED RESPONSES FOR RUGGEDNESS TESTS[a]

Variables	Levels	Response designation	Chloroform		Carbon tetrachloride		Tetrachloroethylene	
			Train 1	Train 2[b]	Train 1	Train 2[b]	Train 1	Train 2[b]
POHC Concentration	0.5 ppb	A_o	1.694	1.656	0.951	0.968	1.208	1.242
	15 ppb	A_1	1.062	1.034	0.782	0.814	1.151	1.117
Moisture	≅ 25%	B_o	1.613	1.556	0.893	0.868	1.257	1.228
	Dry	B_1	1.142	1.134	0.846	0.920	1.101	1.132
Sampling Rate	0.5 l/min	C_o	1.086	1.102	0.843	0.897	1.166	1.234
	1.0 l/min	C_1	1.670	1.588	0.896	0.892	1.192	1.125
Gas Inlet Temperature	≅ 30°C	D_o	1.104	1.068	0.822	0.882	1.250	1.240
	≤ 20°C	D_1	1.651	1.622	0.920	0.906	1.109	1.119
Sorbent Condition	Reused	E_o	1.581	1.638	0.845	0.916	1.104	1.172
	New	E_1	1.174	1.052	0.894	0.873	1.255	1.188
Sample Volume	5 liter	F_o	1.777	1.714	0.906	0.914	1.214	1.132
	20 liter	F_1	0.978	0.976	0.833	0.875	1.145	1.228
Trap Configuration	ST	G_o	1.066	0.985	0.797	0.747	1.156	1.089
	ND	G_1	1.689	1.705	0.943	1.042	1.202	1.270

[a] Each value represents the response calculated using normalized concentrations and the equations in the table of response formulas.

[b] For Run R7 where results for only one train were valid, the one valid concentration was used in the calculation of responses for both trains.

TABLE E-11. SUMMARY OF RUGGEDNESS TEST DIFFERENCES BETWEEN VARIABLE LEVELS FOR CHLOROFORM, CARBON TETRACHLORIDE, AND TETRACHLOROETHYLENE

Variables	Levels	Chloroform				Carbon tetrachloride				Tetrachloroethylene			
		Differences				Differences				Differences			
		Between trains[a]		Between differences	Sum of differences	Between trains		Between differences	Sum of differences	Between trains		Between differences	Sum of differences
		Train 1	Train 2			Train 1	Train 2			Train 1	Train 2		
POHC concentration	Δ0.5-15 ppb	0.632	0.622	0.010	1.25	0.169	0.164	0.015	0.323	0.057	0.125	-0.068	0.182
Moisture	Δ25%-Dry	0.471	0.422	0.049	0.893	0.047	-0.052	0.099	-0.005	0.156	0.096	0.060	0.252
Sampling rate	Δ0.5-1.0 liter/min	-0.584	-0.486	-0.098	-1.07	-0.053	0.005	-0.058	-0.048	-0.026	0.109	-0.135	0.083
Gas inlet temperature	Δ30°-20°C	-0.547	-0.554	0.007	-1.10	-0.098	-0.024	-0.074	-0.122	0.141	0.121	0.020	0.262
Sorbent condition	ΔReused-New	0.407	0.586	-0.179	0.993	-0.049	0.043	-0.092	0.006	-0.151	-0.016	-0.135	-0.167
Sample volume	Δ5-20 liter	0.799	0.738	0.061	1.54	0.073	0.039	0.034	0.112	0.069	-0.096	0.165	0.027
Trap configuration	ΔST-HD	-0.623	-0.720	0.097	-1.34	-0.147	-0.295	0.148	-0.442	-0.046	-0.181	0.135	0.227
	Sum of squares	2.45	2.51	0.057	9.87	0.073	0.117	0.050	0.329	0.078	0.094	0.090	0.252
	σ[b]	0.838	0.848	0.090		0.145	0.181	0.085		0.149	0.163	0.113	
	Math check[c]	X	X			X	X			X	X		
F-test value[d]		173				6.58				2.80			
Condition effects present?[e]		Yes				Yes				Inconclusive			

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[a] Each value represents the difference in normalized responses between Level 0 and Level 1 for given variable.

[b] Standard deviation values shown for trains, taken from the table of normalized concentrations, are based on the eight individual run values. The standard deviations shown for the differences between differences are based on tabulated values; i.e., $\sigma = (\text{sum of squares}/7)^{1/2}$.

[c] Math checks for each train: (sum of squares) x 2/7 = $(\sigma \text{ run values})^2$.

[d] F-test value = (sum of squares for sums of differences)/(sums of squares for differences between differences).

[e] Condition effects are probable if F-test value is greater than $F_{0.90}$ = 2.78 (for seven degrees of freedom in numerator and denominator).

the responses between the two levels for each variable (for example A_0 and A_1) are presented for each duplicate train in Table E-11. For Run R7 where only one value was obtained for these three compounds, the one value was used to calculate the response and difference for both trains. In Table E-11, the third column for each compound represents the variability of the duplicate trains and is the difference of the differences for each variable. The values in the fourth column for each compound are the sum of the differences listed for Trains 1 and 2. This column will magnify the effect when both trains showed the same effect (both positive or both negative) and diminish the effect when the trains showed opposite effects (one positive and the other negative). The values in Columns 3 and 4 are used in the F-test calculations to determine if condition effects are present. The sum of the squares under each column is obtained by squaring each number in the column above it and calculating the sum. The other parameters in the table are explained in the footnotes. The magnitude of the differences for each variable for chloroform are large and condition effects are present according to the F-test value. Closer inspection of the data shows that all of the calculated differences are influenced to a great degree by the result of the 3.41 value in Run R7 (Table E-9). No procedural reason has been determined for considering this value an outlier, but considering that this value corresponds to a 341 percent recovery makes this value highly suspect. Therefore, no conclusion for chloroform will be based on the results in Table E-11.

The results for Runs R1 and R2 (104 and 116 percent EV and 4 percent RSD) were comparable to individual values obtained by similar quad runs (85 to 116 percent EV and 1 to 10 percent RSD, excluding the suspected outlier for Runs Q1 through Q8 and W1 through W8) (see Subsection 4.1.6). Therefore, the differences in sampling rate, sorbent condition, and sample volume between Runs R1 and R2 either had little effect or a balancing effect on measured results. In fact, all of the ruggedness tests yielded similar results for chloroform (85 to 120 percent EV and 1 to 18 percent RSD) except for Runs R7 and R8 (136 to 340 percent EV and 2 percent RSD). Both Runs R6 and R7 were conducted at test conditions of 0.5 ppb, ND train type, and 5-liter sample volume. Because the results of Runs Q6 through Q8 and W5 through W8 indicated that there was no significant difference between ND and ST trains at the 0.5-ppb test condition, and the recoveries at 0.5 ppb were slightly lower than those at 15 ppb, the higher recoveries exhibited by Runs R6 and R7 may be the effect of the 5-liter sample volume or the result of increased significance of blank contamination when less than 20 ng of the compound is collected.

Carbon Tetrachloride--

The results of Youden's data reduction procedure of the ruggedness test data are presented in Tables E-10 and E-11. The F-test value in Table E-11 indicates condition effects are present. Inspection of the differences and a comparison with the standard deviation values of the trains reveals that the differences for the trap configuration are the only ones that are significantly higher than the standard deviation. The negative values obtained for the differences for each train indicate that the ND type trap is more effective in collecting carbon tetrachloride. This same conclusion was reached in three of the four cases tested during the precision and accuracy runs (Q1 through Q8 and W1 through W8).

The data in Table E-11 do not indicate that moisture has an effect, which conflicts with the results of comparisons discussed in Subsection 4.1.6 that clearly indicate moisture affects the performance of the ST trains to measure carbon tetrachloride. As previously noted, one of the limitations in Youden's approach is the inability to distinguish between interactions. Thus, the fact that the ruggedness test data do not point out the effect of moisture is not surprising, because the effect (as shown in Table 4-8) was limited to the ST trains.

A comparison of the ruggedness tests with Runs Q1 through Q8 and W1 through W8 was also made. Results for Run R1 (93 percent EV and 5 percent RSD) were similar to average values for Runs Q1 through Q3 (87 percent EV and 11 percent RSD, excluding the suspected outliers), which were conducted at similar test conditions. The interpretation of the other ruggedness test runs is limited to those involving the ND trains because of the effect of moisture on the ST type trains and the difference between ND and ST trains shown previously by the precision and accuracy runs.

The combined results of Runs R6 and R7 were compared with the combined results of R1 and RR4. In this comparison all parameters within each group of combined runs balanced each other except that Runs R6 and R7 were both conducted at 0.5-ppb concentrations and 5-liter sample volumes, and Runs R1 and RR4 were both conducted at 15-ppb concentrations and 20-liter sample volumes. The previous comparison between quad runs had indicated that the recovery for ND trains at 0.5 ppb was similar to or slightly less than the recovery at 15 ppb. Therefore, the higher recoveries shown by Runs R6 and R7 (99 to 114 percent EV) compared with those for Runs R1 and RR4 (74 to 96 percent EV) may be attributed to the effect of a smaller sample volume (5 liters versus 20 liters) or the small amount of material collected in relation to the blank level.

Tetrachloroethylene--

Results of Youden's data reduction procedure of the ruggedness test data are presented in Tables E-10 and E-11. The F-test value in Table E-11 is inconclusive in regards to the presence of condition effects. No value for a difference is significantly larger than the standard deviation. No definite conclusions can be reached. The fact that no significant condition effects are present is consistent with the results of the previous series of tests.

Results for all of the valid runs ranged from 92 to 141 percent EV and 1 to 21 percent RSD. These values were similar to the range of those exhibited by the precision and accuracy runs (90 to 135 percent EV and 1 to 14 percent RSD, excluding suspected outliers). No effect was attributed to any of the variables.

Vinyl Chloride--

Run R1 was the only ruggedness test sample pair collected at nominal VOST conditions. The results should be comparable to the results of quad Runs Q1 through Q3 for the ND sampling trains; however, the average of 51 percent EV and 25 percent RSD exhibited by Run R1 results do not compare favorably with 91 percent EV and 8 percent RSD for the referenced quad runs (see Table 4-7, 15 ppb, dry). The discrepancy suggests that measurement of VC is difficult for either train type. The highest recovery of VC shown by any of the valid ruggedness tests is 60 percent EV (for one of the R1 samples). Further discussion is not warranted.

Trichlorofluoromethane--

The results for Run R1 (68 to 74 percent EV and 5 percent RSD) compare well with the average 76 percent EV and 6 percent RSD for the ND trains in

Runs Q1 through Q3, which were conducted at similar conditions (see Table 4-7, 15 ppb, dry). Results for Run R2 (49 to 63 percent EV and 18 percent RSD) agreed with the average results of the ST trains for Runs Q1 through Q3 (56 percent EV and 17 percent RSD). Therefore, the difference in variable conditions between Run R2 and the ST trains in Runs Q1 through Q3 probably had either little effect on the results or a balancing effect. These variables were sampling rate, sorbent condition, and sample volume. Results for Runs R5, R6, and R8 were within the range of values obtained for Runs Q6 through Q8 and W5 through W8 (44 to 141 percent EV excluding a suspected outlier); however, this wide range of values makes it difficult to interpret the ruggedness tests. An evaluation of variable levels among Runs R5, R6, and R8 and comparison with the low recovery values in Run R5 and R8 and the high recovery in Run R6 indicate that there is a pattern for only two of the variables: the low recoveries are both obtained when ST trains are used and a sample volume of 20 liters is collected, and the high recovery is obtained only when the ND train is used and a 5-liter sample volume is collected. Because the precision and accuracy runs indicated there was no significant difference between the ND and ST trains at 0.5 ppb, wet or dry, the results suggest that the effect of higher recovery is due to the smaller sample volume, or the result of increased significance of blank contamination when less than 20 ng of the compound is collected.

Benzene--

Results for Runs R1 and R2 (104 to 107 percent EV and 2 percent RSD) are similar to results of quad Runs Q1 through Q3 (100 to 113 percent EV and 1 to 6 percent RSD, excluding suspected outliers). The parameters with values different from those represented by the quad runs include sampling rate, sample volume, and sorbent condition. The effects of these variables, then, are probably slight or they balance each other.

The results for Runs R3 and R6 yielded very high recoveries (222 to 354 percent EV). In examining the combinations of parameters in the other runs, it was found that Runs R1 and R8 had levels of variables that balanced with those in Runs R3 and R6 except that Runs R3 and R6 were both conducted at test conditions of 5-liter sample volumes and gas temperatures of approximately 26°C at the inlet to the first trap. Runs R1 and R8 were both conducted at test conditions including 20-liter volumes and average inlet temperatures less than 20°C. The difference between the combined data for Runs R1 and R8 (104 to 139 percent EV) and for Runs R3 and R6 (222 to 354 percent EV), therefore, may have been related to the different sample volumes, which is also related to the amount collected and the relative level of blank contamination. It does not seem reasonable to expect that the effect of the inlet gas temperature would be significant; however, the potential effect of different sample volumes (or in combination with sampling rates) is not a new idea.*

Summary--

The ruggedness tests supported the conclusion that the ND traps are superior to the ST traps for measurement of carbon tetrachloride. Otherwise, none of the seven variables was shown to have a definite effect on the VOST protocol. The results did confirm that recoveries of benzene can be much higher than theoretically possible when there is less than ∿50 ng of benzene collected in the sample.

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*The Utility of Distributed Air Volume Sets When Sampling Ambient Air Using Solid Adsorbents, Walling, J.F., Atmospheric Environment, Vol. 18, No. 4 pp. 855-859, 1984.

In addition, the results of Runs R6 and R7 (Table E-9) showed that the precision and accuracy produced by the collection and analysis of approximately 10 ng of a compound on a single VOST run are considerably different from those described in Subsection 4.1.6. Whether the combination of several VOST samples (two to four) onto a single trap prior to analysis would improve results at low levels was not determined. Although this is suggested in the protocol, no procedure is given, and the development of such a procedure was beyond the scope of this project.

Another conclusion suggested by the ruggedness tests is that more replications are needed when so many parameters are to be evaluated. Budget and time restraints made this impossible during this laboratory study, but this need should be kept in mind for future tests.